5-2019

Development and Characterization of Extractive Scintillating Resins for Determination of Ultra-Low-Level Plutonium in Aqueous Systems

William Kenneth Fullmer
Clemson University, wfullme@clemson.edu

DEVELOPMENT AND CHARACTERIZATION OF EXTRACTIVE SCINTILLATING RESINS FOR DETERMINATION OF ULTRA-LOW-LEVEL PLUTONIUM IN AQUEOUS SYSTEMS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Science

---

by
William Fullmer
May 2019

Accepted by:
Dr. Timothy A. DeVol, Committee Chair
Dr. Brian A. Powell
Dr. Ayman F. Seliman

ABSTRACT

Extractive scintillating resins (ESRs) simplify quantification of radionuclides from aqueous solutions by reducing the number of steps required and by reducing waste. Two formulations of plutonium ESRs were developed and characterized: (1) by attaching scintillating polymer chains to the surface of a commercially available Pu extraction resin and (2) by impregnating a scintillating resin bead with an organic ligand shown to extract Pu at circumneutral pH. In the first formulation, plastic scintillating polymer was attached to the surface of Pu-02 Analig®, a proprietary silica-based molecular recognition resin developed by IBC Advanced Technologies® for selective aqueous Pu uptake. Batch uptake of the modified resin tests indicated high affinity for ^{242}Pu(IV) from a pH 1 solution (uptake >90%). This resin subsequently was loaded into a perfluoroalkoxy alkane column, and detection efficiency was quantified with a liquid scintillation counter without the introduction of cocktail. On-line measurement with the resin was conducted utilizing a flow-cell radiation detector to quantify the plutonium accumulated on the resin as it was loading on the column. Plutonium quantification with the resins was successful with uptake efficiencies values of >99% and 97% and detection efficiency values of 36.4% and 28.5% for batch and on-line measurements, respectively. Further optimization studies demonstrated that shorter modification times with particles <63μm demonstrated the greatest efficiency for Pu detection and that high concentrations of Fe(III) will interfere with Pu uptake. In the second formulation, dibenzoylmethane (DBM) was investigated for Pu uptake through a series of batch uptake studies and liquid-liquid extractions. Pu(IV) was the primary form to result in uptake with DBM,

however extraction was relatively poor due to hydrolysis and adsorption effects of Pu(IV) at low to circumneutral pH. This was demonstrated when Pu(IV) would adsorb to non-functionalized resin surface to the same extent as a DBM coated surface. When incorporated with a scintillating resin, the DBM significantly quenched light due to absorption of UV wavelengths that are required for fluorophores. Pu selective ESRs are a nuclear forensics tool capable of monitoring water systems for unforeseen releases of plutonium. Given a sufficient counting time of 15 minutes and approximately 300 mL of solution volume, a minimum detection limit capable of meeting the EPA limit for gross alpha activity in drinking water can be achieved with the modified Analig® Pu02 resin.

DEDICATION

To my parents. For providing me the opportunities and encouragement to pursue answers.

ACKNOWLEDGMENTS

I would like to thank, first and foremost, my advisor Dr. Timothy DeVol. When I accepted this position, I was initially overwhelmed and unfamiliar in the realm of radiation detection, polymer science, and radiochemistry. His patience and encouragement allowed me to overcome my concerns and contribute to a community that I had no idea existed as of three years ago. I am an improved researcher, worker, and student because of him.

I would like to thank my committee members Dr. Ayman Seliman and Dr. Brian Powell. Dr. Seliman always took time out of his busy research and work schedule to help me become more efficient with lab techniques and develop concise experimental designs. I am inspired by his work ethic. Dr. Powell knew plenty about plutonium and if there is one thing I learned, it is that plutonium is complicated and I am glad an expert like him was nearby.

I am grateful to work have worked with Dr. Valery Bliznyuk, Dr. Scott Husson, Dr. Nate Conroy, Amruta Pujari, James Foster, Abenazer Darge and all other members of the research group and department. Your collective impact helped me in all aspects of my research and development.

Lastly, I would like to acknowledge my fiancé Ciara. Her support was critical and I could not have made it through without her. Thank you for being there to listen ad nauseam about all my research successes and failures.

This work was supported by the Department of Energy National Nuclear Security Administration Stewardship Science Academic Alliances #DE-NA-0002920 to Clemson

University. The imaging reported in this thesis was performed by Rhonda R. Powell, using a Leica SPE Confocal, housed in the Clemson Light Imaging Facility (CLIF). CLIF is supported, in part, by the Clemson University Division of Research, NIH EPIC COBRE Award #P20GM109094, and NIH SCBiocraft COBRE Award #5P20RR021949-03. The content of this material and any opinions, findings, conclusions, or recommendations expressed in this material is solely the responsibility of the author and does not necessarily represent the official views of the National Institutes of Health.

TABLE OF CONTENTS

Page

Table of Contents (Continued)

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

List of Figures (Continued)

Figure **Page**

List of Figures (Continued)

Figure **Page**

List of Figures (Continued)

Figure **Page**

CHAPTER ONE

INTRODUCTION

The advent of nuclear technology has resulted in advancements to energy production and weapon development. Although controversial, the realities of human exposure from the nuclear industry are ever present with concerns ranging from nuclear fallout to ingestion of trace radionuclides in drinking water. Plutonium-239 is a radionuclide of profound concern, due to it being the primary fissile isotope in nuclear weapons and long-lived radionuclide that has shown to be released or transported into environmental systems (Choppin, 2006; Ewing, 1999). Plutonium-239 decays to ^{235}U by emitting an alpha particle. Excessive ingestion of alpha-emitting radionuclides can be severe and could lead to DNA damage resulting in cancer or other adverse health effects (Cember & Johnson, 2009). Due to the combination of health and national security concerns, developing techniques of monitoring and detection of Pu is of paramount importance.

Great strides have been developed by researchers in recent years to measure and detect radionuclides in environmental systems. One such technology are extractive scintillating resins that have the ability to quantify ultra-trace levels of radionuclides in aqueous samples (DeVol et al., 2000; Duval et al., 2016; Grate et al., 2008; Roane & DeVol, 2002; Seliman et al., 2017). The resin acts as both an extractor of target radionuclide and as a transducer of ionizing radiation into light which can then be recorded. The primary advantage of the extractive scintillating resin is that its use can be expanded into on-line measurements where one can quantify radioactivity being

accumulated in real time. Having an ability to accurately account and measure plutonium in water systems simply in the field could have immediate benefits for public safety protocols ranging from emergency radioactive releases to fallout from perceived foreign threats. Currently, no such system exists. Thus, the subject of this thesis will expand upon the development and characterization of two extractive scintillating resins for measurement of aqueous plutonium.

CHAPTER TWO

BACKGROUND

2.1 Plutonium history

Almost all forms of Pu can largely be attributed to anthropogenic means of the nuclear industry as only ultra-trace amounts of Pu have been found in nature (Runde & Neu, 2011). In 1941, ^{238}Pu ($t_{1/2}$ = 87.7 years) was first discovered at the University of California, Berkeley through bombardment of ^{238}U with deuterons (Clark et al., 2008). Over the next few years, other isotopes like ^{239}Pu ($t_{1/2} = 2.4x10^4$ years) and ^{242}Pu ($t_{1/2} = 3.73x10^5$ years) were discovered through neutron absorption of ^{238}U (Clark et al., 2008). A summary of common Pu isotopes is described in **Table 1**. The most important isotope is ^{239}Pu which is fissile and most prominent isotope in most Pu nuclear waste (Ewing, 1999).

***Table 1**: Summary of common Pu isotopes (Katz et al., 1986).*

Isotope	Half-life (years)	Decay method	Production Method
^{238}Pu	87.7	α	^{238}U
^{239}Pu	2.411 x 10^4	α	^{239}Np daughter
^{240}Pu	6.561 x 10^3	α	multiple and capture
^{241}Pu	14.35	B > 99.99 % α 2.45x10^{-3} %	multiple and capture
^{242}Pu	3.75 x 10^5	α	multiple and capture

Nuclear technology advanced dramatically over the 20th century through a combination of nuclear arsenal buildup and nuclear energy development. By 1996 worldwide Pu inventory was estimated to be 1,350 metric tons and growing (Ewing, 1999). Large quantities of radioactivity were generated and released to the environment

in a variety of ways. Over 2400 worldwide nuclear detonations released an estimated 3,500 kg of Pu in atmospheric tests and 100 kg of Pu released in underground tests (Runde & Neu, 2011). Rocky Flats Plant fabricated uranium and plutonium components for the U.S. nuclear weapons program during the cold war. During operations, significant amounts of radioactivity were released to the air, water and soil around the site (Runde & Neu, 2011). One leak from waste drums resulted in approximately 19,000L or 5.3 Ci of Pu released to the environment and contaminating the subsurface (Clark et al., 2006). The Hanford Nuclear Site previously generated plutonium for the atomic bomb and had significant releases of radionuclides into the soil and water systems throughout the years (Alvarez, 2005). Currently, 210 kCi of Pu are held in radioactive waste tanks from early separation years at Hanford (Alvarez, 2005). Currently, 140 million liters of actinide containing salt solutions and sludges are stored in 49 tanks at the Savannah River Site (Runde & Neu, 2011). Not only do the leaks pose a threat to the immediate vicinity, but studies have shown Pu is capable of traveling long distances. At the Nevada National Security Site, Pu had been shown to traverse its way 1.3 km through the subsurface into groundwater systems as a colloid (Kersting et al., 1999; Kersting, 2013). Pu concentrations in the aqueous systems have been recorded at locations distant from their origination of release. For example, ^{239}Pu concentration ranges of 7.7×10^{-3}–2.8×10^{-4} Bq/L and 2.3×10^{-2}–4.2×10^{-4} Bq/L have been reported in surface and groundwaters at Rocky Flats Plat and Nevada National Security Site, respectively (Kersting & Zavarin, 2011; Santschi, et al., 2002).

2.2 Plutonium chemistry

Plutonium has complex chemical attributes where some processes such as chemical complexation and redox influences are still not quite well understood. Plutonium is an actinide with a unique and complex chemical nature to the interplay of the 5f electron shell (Katz et al., 1986). This allows Pu to have a multitude of oxidation states with the (III), (IV), (V), and (VI) species simultaneously existing in most environmental systems (Kersting, 2013; Silva & Nitsche, 1995). Plutonium is unique in that it has a sensitive redox nature where slight chemical alterations in pH and Eh can heavily influence the oxidation state (**Figure 1**). To mitigate Pu redox changes, stable actinide analogues of Am(III), Th(IV), Np(V) and U(VI) are substituted in experiments for their respective Pu redox species (Choppin, 2006; Kaplan et al., 2004; Saito & Choppin, 1983). This is because many of the actinides of the same oxidation states tend to have similar chemical behavior (Silva & Nitsche, 1995).

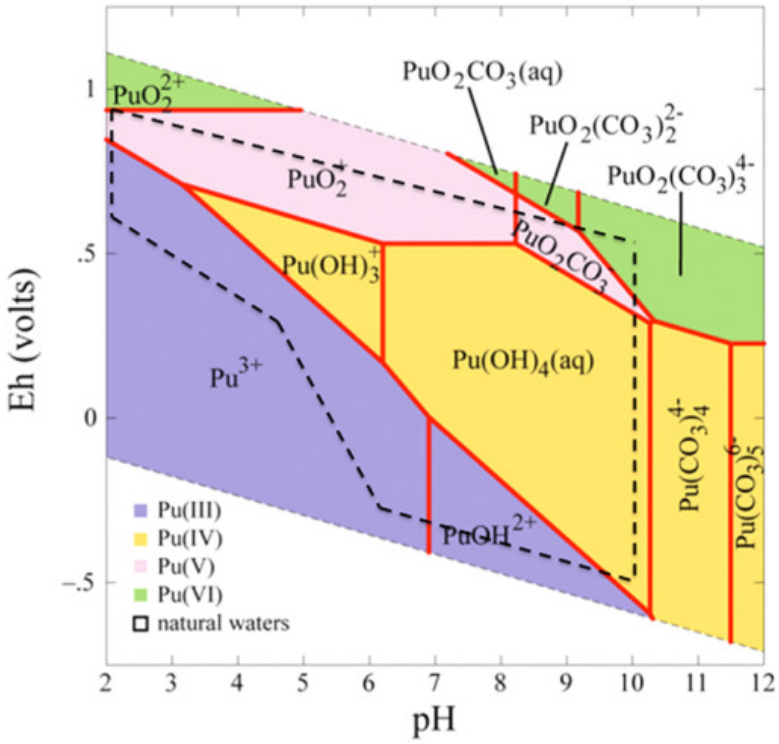

Figure 1*: Example of a Pourbaix diagram for Pu simulated with $NaHCO_3$ and $10^{-3.4}$ bar of CO_2 at 25°C* (Kersting, 2013).

Oxidation states of Pu in environmental systems often exist simultaneously together and the oxidation states often dictate behavior like complexation and sorption (Kersting, 2013). It is expected that Pu(III) and Pu(VI) commonly exist in environmental conditions; however, the majority of Pu speciation in groundwater and surface water will consist of Pu(IV) and Pu(V) (Choppin, 2006; Nash et al., 1988). In natural waters (pH 4-9 and -0.2 to +0.6 V) the most dominant aqueous-phase oxidation states are predicted to be Pu(III), Pu(IV), and Pu(V) (Hixon & Powell, 2018). These Pu species can form common inorganic complexes such as $Pu(OH)_4$, PuO_2^+, and $PuO_2CO_3^-$ in many natural waters (Runde et al., 2002). Additionally, Pu has also shown to complex with citric acid and other natural organic matter (Conroy, et al., 2017).

Plutonium (IV) has high affinity for surface sorption and complexation, while Pu(V) will be remain in the aqueous suspension. The behavior is due to the effective charge of Plutonium ions and oxygens present on the actinyl ions. The strength of complexation or sorption follows: Pu(IV) > Pu(VI) > Pu(III) > Pu(V) (Kersting, 2013; Silva & Nitsche, 1995). Plutonium (IV) often controls the speciation of a system due to Pu(V) being influenced by the equilibrium partitioning of Pu(IV) sorption and complexation and can result in a reduction of Pu(V) to Pu(IV). This may be a slow process as Pu(V) is an actinyl ion (PuO^{2+}) that is required to undergo substantial chemical change by breaking the two axial oxygen bonds (Choppin, 2006; Powell et al., 2004). In addition, Pu(V) has been shown to reduce to Pu(IV) in presence of organic and mineral surfaces (Conroy et al., 2017; Powell et al., 2004). It can be expected in most environmental waters that Pu(V) will be the mobile phase and Pu(IV) will be immobile sorbed to surfaces, however, this is not always the case. Pu(IV) has been shown to undergo facilitated transport via colloid transport with sediment, organic matter or as an intrinsic colloid (Conroy et al., 2017; Kaplan et al., 2004; Kersting et al., 1999; Kersting, 2013). Thus, it is important to consider concentrations of colloidal and solid concentrations when implementing an analytical method for interpretation of Pu in waterbodies.

2.3 Plutonium extraction and separation techniques

Early separations of radionuclides utilized the concept of precipitation to separate nuclides. Common precipitation methods for separating Pu consisted of $BiPO_4$ (Hill &

Cooper, 1958) and LaF_3 coprecipitation (Kobashi et al., 1988). Over time, liquid-liquid solvent extraction became a common method for concentrating and separating various radionuclides (Choppin & Morgenstern, 2000). This allowed for continual concentration into small volumes that could easily be managed. The process involves the preferential transfer of analyte between two immiscible solvents given sufficient contact. One of the most common solvent extraction methods is the PUREX process where Pu and U are separated from mixed waste streams in a large-CMA process with ligand tributyl phosphate (TBP) in kerosene (Choppin & Morgenstern, 2000; Flanary, 1954).

More recent developments with solvent extractions have allowed the ability to separate Pu based on redox state. These extraction schemes take advantage of pH and kinetics to allow separation by redox state. Most notably, common polydentate organic anion such as thenoyltrifluoroacetone (TTA), 4-benzoyl-3-methyl-l-phenyl-2-pyrazolin-5-one (PMBP), di-2-ethylhexyl phosphoric acid (HDEHP), and dibenzoyl methane (DBM) (Choppin et al., 1997; Conroy et al., 2016; Neu et al., 1994; Saito & Choppin, 1983; Schramke et al., 1989) and large polydentate cations like diglycolamide (DGA) (Sasaki et al., 2000; Van Hecke & Modolo, 2004) have been deployed in Pu speciation separations. Dibenzoyl methane (DBM) has been used in many Pu extraction and oxidation analysis methods (Coates et al., 2001; Kobashi et al., 1993; Saito & Choppin, 1983). It is a polydentate anion that forms neutral complexes with actinides. High uptake with DBM has been observed at low to circumneutral pH based on the given oxidation state with An(IV) having highest uptake (**Figure 2b**). By manipulating redox and solution chemistry, a Pu extraction scheme was developed through a series of liquid-

liquid extractions using DBM (Saito & Choppin, 1983). The two phenyl groups on DBM allow for a likely transformation into a monomer that can be polymerized (**Figure 2a**).

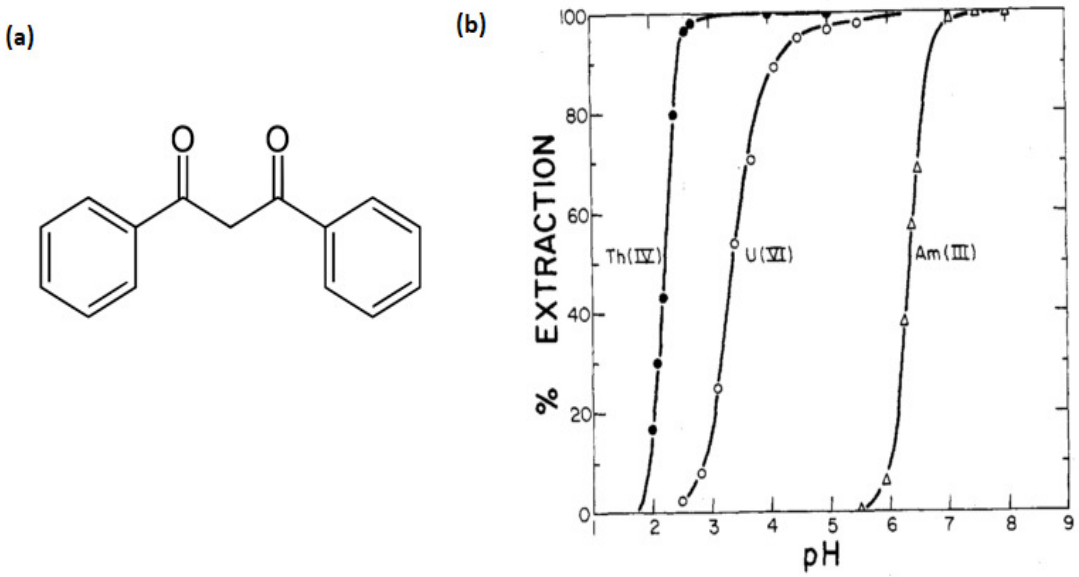

Figure 2: *(a) structure of the dibenzoylmethane (DBM) molecule. (b) Uptake of various actinides with 0.2M DBM in benzene with liquid-liquid extraction* (Saito & Choppin, 1983).

Extraction chromatography is a common method for extraction of radionuclides. It is a technique that combines selectivity of solvent extraction with simplicity of column chromatographic methods (Horwitz et al., 2006). An inert, porous resin bead is impregnated with an organic phase with analyte-specific ligands (**Figure 3**). These resins are advantageous because they produce less waste compared to solvent extraction methods and can be easily managed. They are often packed into columns and can be stacked upon another to allow a variety of extraction and elution schemes (Gostic, 2009; Horwitz et al., 1995; Kazi et al., 2014). Eichrom Technologies, Inc. (Darien, IL, USA) has been the primary developer of these extraction chromatography resins and provides

many commercially available products. Some of the most notable extraction chromatographic resins for actinides and Pu are the TEVA, TRU, and DGA resins (Horwitz et al., 1995; Maxwell, 2006).

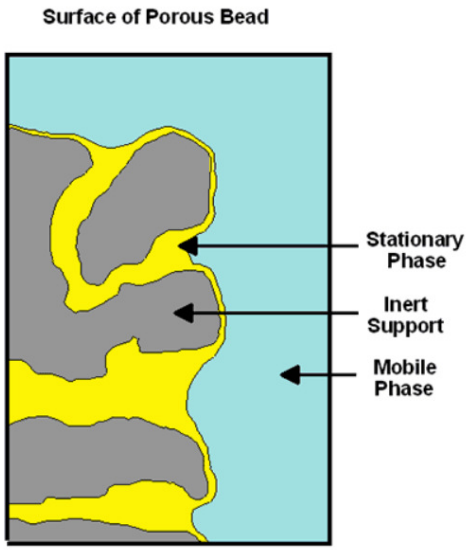

***Figure 3**: Example of chromatographic resin (http://www.eichrom.com/products/extraction.aspx).*

New technologies for radionuclide extraction have emerged in the field of solid-phase extraction. As the name suggests, these resins have the ligand chemically attached to the resin bead in a variety of ways. Many companies utilize molecular recognition technology (MRT) to develop a complex host-guest system. This "host-guest" recognition technology allows for the design of a resin to be specifically built around a target analyte where speciation, solution matrix, pH and other ions are considered (Izatt et al., 2003). These solid-phase resins are valuable as they can extract trace quantities of an analyte in complex waste streams where common interfering ions are present (Izatt et al., 2003).

One such solid-phase extraction resin is Pu-02 Analig®. It is a proprietary resin developed by IBC Advanced Technologies® using MRT for selective Pu(IV) uptake. The structure of the Analig® Pu02 resin is primarily composed of silica with proprietary ligands attached to the base. It is a robust resin that can handle pH values below 9.5 and is commonly used in solutions with several molar acid concentrations (Dulanská et al., 2012; Dulanská et al., 2011). Previous studies show high Pu uptake and recovery in contaminated sludges with results comparable to TRU resin in samples with less than 200 mg of Fe^{3+} (Dulanská et al., 2011).

2.4 Plutonium detection with liquid scintillation counting

Once a target Pu isotope is successfully isolated through chemical means, it can undergo a series of measurement or detection techniques. Common methods of quantifying concentration or activity are through mass spectrometry, alpha spectroscopy, and liquid scintillation counting (LSC) (Grate et al., 2008). Mass spectrometry and alpha spectroscopy allow for the ability to differentiate among the various types of Pu isotopes. This is a valuable tool, because chemical separations are independent of the isotope and mixed distribution of Pu isotopes could largely impact experiment design. Liquid scintillating counting is a useful radiochemistry technique that can be used to obtain activities when the isotope is generally known. In liquid scintillation counting, an aliquot of Pu sample is inserted into a LSC cocktail solution. The cocktail solution is often composed of organic solvent, emulsifier, and fluor. The alpha particle kinetic energy is transformed into visible light through a series of excitations and deexcitations of the

cocktail molecules. The light is detected by photomultiplier tubes (PMT's), often in coincidence. Because of the high LET of the alpha particles, the detection efficiency for LSC is approximately 100%. Sometimes, quenching due to chemical or color effects will result in a lower detection efficiency and should be considered in experimental design and interpretation.

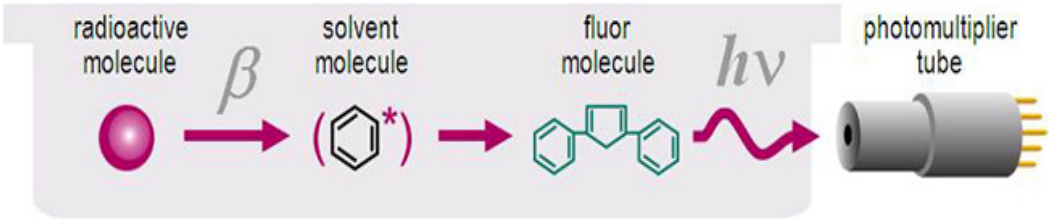

Figure 4: *Schematic overview of the scintillation process* (PerkinElmer, 2007).

2.5 Extractive scintillating resins

Extractive scintillating resins have been developed to combine both extraction and detection. These resins have scintillator material incorporated within the resin matrix which consist of a plastic base and fluor (Duval et al., 2016; Seliman et al., 2017). The plastic base will absorb the kinetic energy from the alpha particle where a resulting phonon will transfer energy to the fluor. The fluor will then excite/deexcite with emission of visible light. The light can be measured using photomultiplier tubes where the intensity of light is proportional to the initial decay energy of a radionuclide. Due to the short range of alpha particles, it is necessary that the radionuclide be as close as possible to the scintillator (Duval et al., 2016). As a result, the small resin particles are often packed tightly into a column to ensure interaction with the ionizing radiation. Additionally, a ligand with high Pu affinity is incorporated within the resin matrix or

chemically attached to extract Pu from solution. This allows the alpha particle to interact with the scintillator. The number of interactions within a given window of time can then be used as a counting system to find total activity loaded onto the resin once efficiency calculations are factored in.

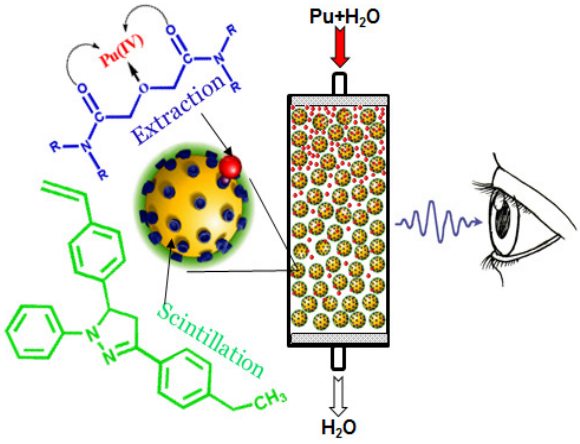

Figure 5*:Example of an extractive scintillating resin column* (DeVol & Husson, 2018).

Early extractive scintillating resins resembled extraction chromatography resins where the extractant and fluor was physically impregnated within the resin bead (Devol et al., 2000; Grate et al., 2008; Harvey et al., 1998; Roane & DeVol, 2002). These resins were tested separately and simultaneously on several radionuclides emitting alpha and beta particles that could be eluted based on oxidation state and equilibrium parameters (Roane & DeVol, 2002). Roane and DeVol (2002) achieved 77% to 95.5% detection efficiency with an extraction chromatography resin for a solution containing multiple actinides. One of the actinides was ^{239}Pu(IV) in 2M HNO_3. Additionally, DeVol (2000) also achieved 100% uptake and detection efficiency for ^{241}Am with scintillator and

extractant impregnated within a styrene-based polymer. Recently, extractive scintillating resins have distanced themselves from the design of extraction chromatography resins by chemically incorporating the fluor and extractant within the resin (Bliznyuk et al., 2015). Stability of the resin was increased by covalently incorporating all components of the extractive scintillating resin. Several examples include extractive scintillating resins for detection of U(VI) (Duval et al., 2016) and ^{90}Sr (Seliman et al., 2017).

CHAPTER THREE

OBJECTIVE

The main objective of this study is to investigate new extractive scintillating resins that are capable of low-level Pu detection. Two approaches will be performed to address this objective.

Approach 1: *Modification of a commercially available Pu extractive resin.*

- Analig® Pu02 will undergo a surface modification where scintillator will be grafted and polymerized on the functional silica surface.
- The modified resin will be characterized through a series of uptake and radioluminosity experiments.
- The modification will be performed several times to ensure reproducibility.
- Parameters of the modification procedure will be examined to optimize the performance of the modified resin.
- Column size and materials will be investigated to examine their influence on radioluminosity.
- Potential environmental interferences will be investigated for Pu uptake.
- The modified Analig® Pu02 resin will be used for on-line Pu detection using a flow cell adapted with photomultiplier tubes.

Approach 2: *Characterize a DBM scintillating extraction chromatography resin*

- Liquid-Liquid extractions will be performed to characterize Pu uptake with DBM by examining factors like solvents, pH, and redox influences.
- A DBM extraction chromatography resin will be developed and characterized for Pu uptake.
- A scintillating DBM extraction chromatography resin will be developed and will be characterized for Pu uptake and radioluminescence.

CHAPTER FOUR

MATERIALS AND METHODS

4.1 Methods for Analig® Pu02 modification

4.1.1 Analig® *Pu02 modification*

Scintillator was incorporated with the exposed Analig® Pu02 resin in a two-step process of (1) silanization followed by (2) surface-polymerization (**Figure 6**). The Analig®-Pu02 resin was exclusively designed for Pu extraction, therefore requiring attachment of scintillator for detection purposes. Previous efforts were successful with ^{90}Sr based off of the work of Seliman et al. (2017). The Analig®-Pu02 resin, like the ^{90}Sr resin which was also developed from IBC Technologies Inc., is primarily composed of silica. These similarities indicated that the modification method performed with the Analig®-Pu02 resin would likely work. The first step consisted of a silanization reaction using 3-methacryloxypropyltrimethoxysilane (MPS) to promote formation of vinyl groups on silica surfaces. The raw Analig® Pu02 resin beads were suspended in toluene with addition of MPS and stirred for up to 24 hours with an overhead stirrer (IKA® RW 11) in open atmosphere with no heat. The suspension was then filtered and washed with toluene and ethanol. After washing, the silanized resin was allowed to dry for a minimum of one day in a lab hood.

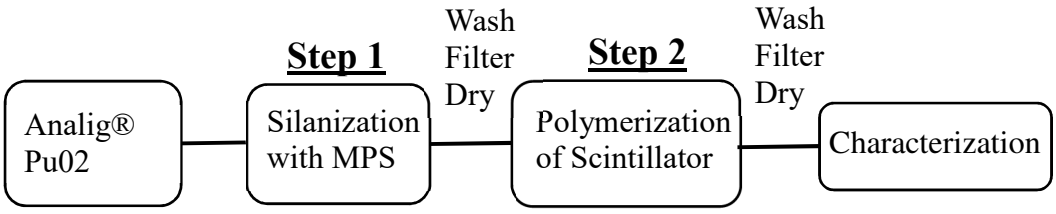

Figure 6: *Simplified schematic of Analig® Pu02 modification procedure.*

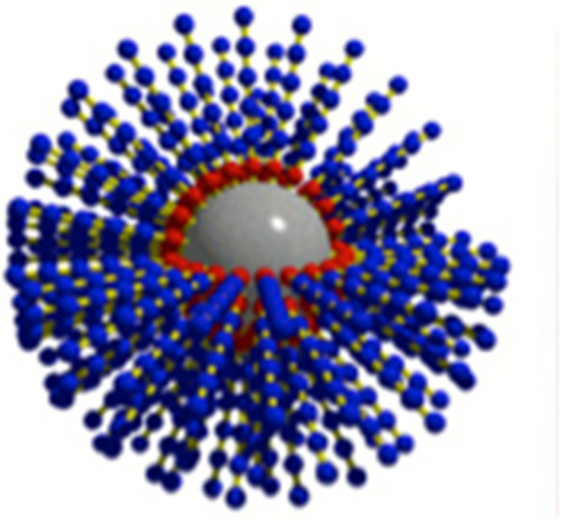

Figure 7: *Analig®Pu02 resin (grey) with grafted scintillating polymer chains (blue)* (Matyjaszewski, 2016).

The second step consisted of grafting scintillator material to exposed surfaces with continual growth of the scintillating polymer chains (**Figure 7**). The scintillator consisted of a combination of polyvinyl toluene (PVT) and a fluor monomer that was copolymerized simultaneously. PVT had been shown to be more stable than polystyrene (Duval et al., 2016) and was made from the methylstyrene monomer (98% stabilized, Arcos Organics) previously conditioned with alumina to remove inhibitor. The fluor, 2-(1-naphthyl)-4-vinyl-5- phenyloxazole (vNPO), was chosen as it is stable in most conditions (Duval et al., 2016) and was specifically designed to be polymerized with an extractive resin for optimal detection using PMT's (Seliman et al., 2015) . The fluor, monomer, and silanized resin were added to a 200 mL round bottom flask. Toluene was added and the mixture was stirred. Azobisisobutyronitrile (AIBN, 98% Sigma Aldrich), an initiator, was then added to the mixture. The mixture was bubbled with nitrogen gas for 15 minutes. The solution was heated, stirred with an overhead mixer (IKA® RW 11),

and refluxed for approximately one day at 70°C. The setup is shown in **Figure 8**. The solution was then filtered and washed with toluene and ethanol. The resin was then dried for approximately one day. Once ready, the modified Analig®Pu02 resin was then characterized by conducting uptake and luminosity measurements.

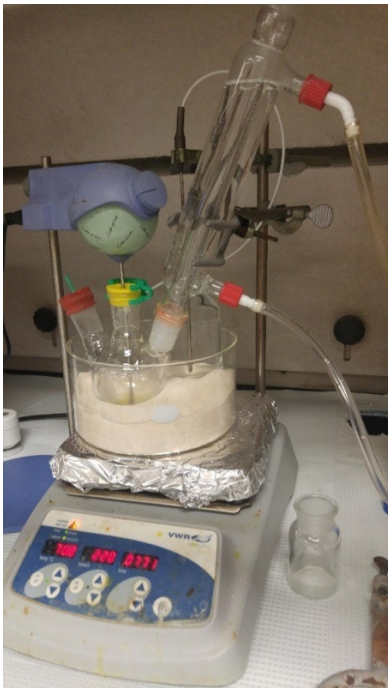

Figure 8: *Set-up for the polymerization and attachment of scintillator to the silanized Analig® Pu02.*

4.1.2 Batch uptake

Batch experiments were the primary method for obtaining initial uptake results. Essentially, a given resin mass was mixed with a specified volume of solution consisting a known activity (**Figure 9**). The majority of experiments used approximately 10 mg of resin with 3 mL of Pu solution. The solution and resin beads were then mixed for a given time in a 15 mL polypropylene falcon tube for various time amounts. After mixing, the

resin beads were centrifuged or allowed to settle out suspension. If settling was not possible, the samples would be filtered with a 0.45 μm Nylon filter as long as filter sorption effects were minimal. Next, a volume of supernatant (≈1 mL) was collected and placed into a 20 mL glass LSC vial with 10 mL of LSC cocktail (Ultima Gold™ or Ultima Gold™ AB). The sample was counted by Quantulus 1220 (Perkin Elmer) LSC for a set time to obtain desired statistical confidence. Counts times of 15 minutes would often give approximately 3% statistics. Detailed experimental parameters used in uptake experiments are described in the results section for each experiment.

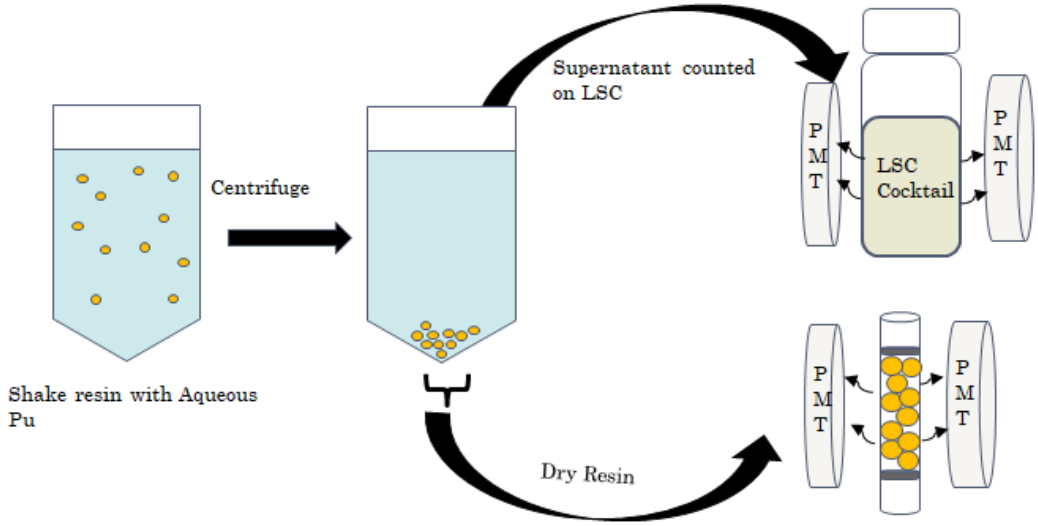

Figure 9: *Schematic for batch uptake and luminosity experiments.*

Batch uptake experiments were used to obtain parameters like uptake efficiency (ε_u) and the radionuclide distribution coefficient (K_d). ε_u is defined as the fraction of activity that was removed from the aqueous phase by the resin. The uptake efficiency only provided information relating the initial concentration (C_0), or activity (A_0), to the

final concentration (C_e), or activity (A_e). This parameter is often simple and easy to understand; however, it provides little information regarding the volume and mass ratios used in the experiment. The K_d value normalizes these mass and volume ratios to express the extent of uptake that agrees more with the experimental batch setup (Seliman, 2012). This value is often expressed as (mL/g). It should be cautioned that sometimes it can exaggerate the degree of uptake and error when poor uptake and or near-complete uptake are observed.

$$\varepsilon_u = 1 - \frac{A_e}{A_0} \quad (1)$$

$$K_d = \frac{\varepsilon_u}{1 - \varepsilon_u} * \frac{Volume\ (ml)}{Sorbent\ Mass\ (g)} \quad (2)$$

Often times, Pu(IV) would sorb to container walls or precipitate out of solutions at higher pH. To account for wall-sorption in uptake experiments, an additional step was required. Both solution and resin were removed from the container by a combination of decanting and addition of a background solution (no activity) to suspend hard-to-remove resin that was unable to be decanted. This background solution had similar solution chemistry that would help minimize establishment of a new equilibrium. Next an acidic solution of 0.1M HNO_3 or higher strength was added to the vessel and mixed for 24 hours. After mixing, the supernatant was counted by LSC and used to calculate A_{wall}, the activity sorbed to the container walls. This value was used to calculate the recovery

(**Equation 3**) of Pu in most experiments where A_{ligand} is activity bound to the extractive resin.

$$Recovery = \frac{A_e + A_{wall} + A_{ligand}}{A_0} \quad (3)$$

4.1.3 Column experiments

Column experiments were conducted to examine uptake characteristics where the resin and solution were not continually mixed. Here, column flow experiments resemble real world applications and can approximately mimic plug-flow regime. To prepare the columns, approximately 10 to 50 mg of resin was packed into a plastic PFA tube with a 1/16-inch inner diameter. The resin mass varied, but a 5cm length of column tubing was common, as this was the maximum length for a single coil for radioluminosity measurements in the Beta-Ram instrument. Greater than 5 cm lengths could be achieved through folding and compressing into various geometric coil shapes for PMT detection, however this was not needed for these experiments. The plastic PFA column had glass wool inserted to retain the resin beads. A background solution was pumped through for a given volume to allow proper conditioning and filling of pore space. Activity was then pumped through where the effluent was collected and then subsequentially counted by LSC. The uptake was calculated based on the difference between influent and effluent concentrations. The collection of effluent was carefully considered as breakthrough of resin could occur and thus fractions were collected over. The two types of pumps used were the Beta-Ram (Lab-Logic) and a Tandem Model 1081 (Sci-Log Inc).

4.1.4 Off-line measurement

Off-line measurements were conducted by performing radioluminescent measurements on Pu-loaded resins from batch reactions. These measurements provided initial results of the detection efficiency, ε_d, of the resins (**Equation 4**). This was accomplished by collecting the Pu-loaded resins after batch contact and inserting them into a 5 cm long PFA tube. The resin was packed wet, by pipetting the resin beads at the bottom of the falcon tube and then carefully inserting them into the column. The columns had glass wool located at the bottom to capture the loaded resin beads. Often, the mass used in the uptake experiments was much lower than occupying 5cm of column space, so only a fraction of the column was occupied by loaded resin. After packing, the column was placed in a lab hood and allowed to dry for several days. The mass of column was recorded daily until a stable mass was determined. Next, the columns were placed in 20 mL LSC vials, without the introduction of liquid scintillation cocktail, and counted with the Quantulus 1220 LSC (**Figure 10**). The columns were dark-adapted to ensure that light was solely due to radiation. A blank column was always counted for each Pu-loaded column to calculate net counts. The blank was made by exposing the resin beads to a background solution with the same solution chemistry. The non-Pu-loaded beads were inserted into the column and allowed to dry in the same way as the Pu-loaded columns. The blank resins were always counted simultaneously as the Pu-loaded

resin. The total detection efficiency (ε_t) as determined by multiplying products of detection efficiency and uptake efficiency (**Equation 5**).

$$\varepsilon_d = \frac{Count\ rate\ detected\ by\ LSC}{A_{Ligand}} \tag{4}$$

$$\varepsilon_t = \varepsilon_u \times \varepsilon_d \tag{5}$$

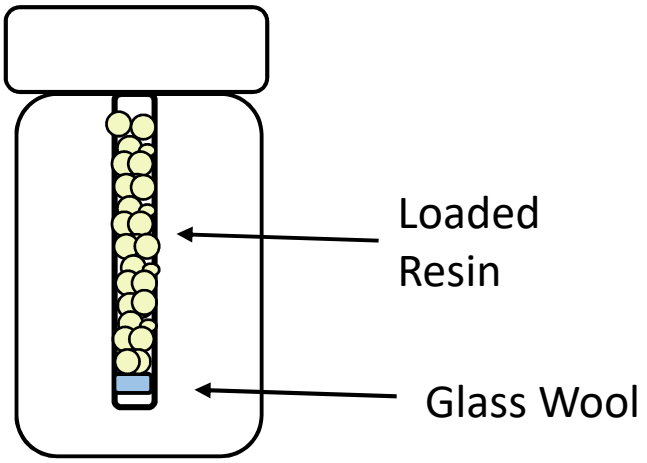

***Figure 10**: Example of a column positioned into a 20mL glass LSC vial.*

The minimum detectable activity concentration (MDC) was utilized to infer information on real world detection limits of the resins. It is a valuable parameter that can be used to compare against regulatory standards. The MDC formula is described by **Equation 6** where C_b is the background count rate, t is counting time, ε_t is the total efficiency, and V is sample volume.

$$MDC = \frac{2.71 + 4.65\sqrt{C_b * t}}{t * \varepsilon_t * V}\ Bq/mL \tag{6}$$

4.1.5 On-line measurement

Real time Pu detection was performed with the Beta-Ram instrument. The set-up implemented column flow, but also allowed for radiation detection (**Figure 11**). A 17cm PFA column with 1/16" inner diameter was packed with 5 cm of resin held with glass wool. The column was inserted into the holding cell of the instrument and dark adapted overnight. A 10 mL background solution of 0.1M HNO_3 was then pumped through to condition the column. After conditioning, a ^{242}Pu solution with approximately 10 Bq/mL activity was pumped through and subsequentially followed by 10 mL of a conditioning background solution to observe a stable reading. Effluent was collected in aliquots and counted by LSC. The scintillation light was recorded by PMT's in the Beta-Ram instrument and data was analyzed through the Laura™ radiochromatography software from LabLogic Company. Flow rates for the columns ranged from 0.2-1 mL/min and were determined by running a background solution before the experiment to allow for filling of pore space.

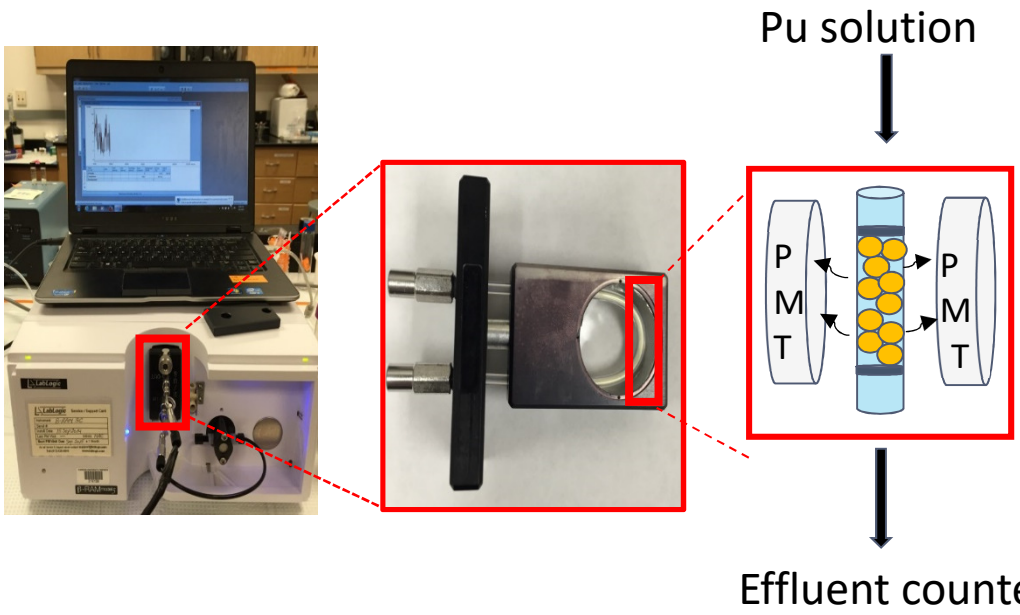

Figure 11: *Beta-Ram model 5 instrument with data collection from Laura™ software. The mixing cell showing the 5cm resin column. Pu solution is pumped through the resin column and detected with PMT's.*

4.1.6 Confocal microscopy

Confocal microscopy allowed for imaging of the spatial distribution of scintillator attached to the Analig® Pu02 resins. A laser excites the scintillator allowing emission of light that can be processed by a PMT detector. Resin samples were deposited in the wells of a LabTek coverglass chamber slide and imaged using a Leica SPE confocal microscope (Leica Microsystems, Buffalo Grove, IL), equipped with a traditional PMT detector. Imaging was conducted using an excitation wavelength of 405 nm and emission wavelengths of 410-480 nm, and a 10X objective (N.A.= 0.3) with a zoom of 1.5. The 405 nm wavelength was chosen based on similar procedures for other extractive scintillating resins (Duval, et al., 2016) and was the lowest wavelength laser available. Imaging conditions (gain, laser power, offset) were held constant so that relative

fluorescence intensity comparisons could be made. A differential interference contrast (DIC) image was also collected for each sample to identify the basic structure of the beads in the absence of fluorescence.

4.2 Methods for DBM resin

Several methods that were employed for the Analig® Pu02 modification were also used is the characterization of the DBM resin. They include batch uptake, off-line detection, and column uptake. For more information these methods and techniques please see **Section 4.1**.

4.2.1 Liquid-liquid extractions

Liquid-Liquid extractions were used for examination of Pu uptake and operated based on differences of density and miscibility. Approximately 0.6 mL of organic solvent containing an actinide specific ligand was inserted into a 1.5 mL polypropylene tube. An equal volume of aqueous solution containing Pu was next added. The two phases were shaken by hand or shaker for a given amount of time to ensure proper transfer. The length of shaking was dependent on the equilibrium chemistry of each phase, with longer shaking time ensuring greater transfer to organic phase as long as steady state was not reached. Common mixing times ranged from 5 to 15 minutes. The mixed solution was then centrifuged for 5 minutes to allow proper separation of phases. The organic phase was less dense than water, and was collected by first inserting a pipette tip into the organic phase without disturbing the aqueous phase. The exacted volume was

recorded and placed in a 20 mL LSC vial. Next, a different pipette tip was inserted through the remaining organic phase while the tip was blowing out air bubbles. This was to ensure no organic was in the pipette tip. The pipette tip was placed at the bottom of the vessel and the aqueous solution was collected and volume recorded. The solutions were then counted by LSC to determine activity in each phase. After calculating uptake parameters, a recovery calculation (**Equation 3**) was performed to make sure that no Pu was lost and that the procedure was performed correctly.

4.2.2 Oxidation state analysis

Determination of oxidation state, primarily Pu (IV,V,VI), was performed by liquid-liquid extraction and coprecipitation (**Figure 12**). The liquid-liquid extraction utilized 0.025M 4-benzoyl-3- methyl-1-phenyl-2-pyrazolin-5-one (PMBP) in heptane and 0.5 M bis(2-ethylhexyl)-phosphoric acid (HDEHP) in heptane. The Pu solution was adjusted to low pH with addition of 1M HCl and mixed with the organic phase. A liquid-liquid extraction was performed to observe the partitioning of activity in the two phases. Pu(V) would remain in the aqueous phase while PMBP would extract Pu(IV) and HDEHP would extract both Pu(IV) and Pu(VI). The difference between HDEHP and PMBP would account for the fraction of Pu(VI) in solution. A LaF_3 coprecipitation was used a confirmation check to assure that experiment was performed correctly. Here, 1 mL of 0.01M $La(NO_3)_3$ and 0.5 mL Pu solution were added to a 2 mL polypropylene vial. 10 μL of concentrated HF was added to the mixture and the sample was gently mixed for 2 minutes. The Pu(IV) and La(III) would precipitate with the fluoride ion

leaving Pu(VI) and Pu(V) in solution. The mixture was centrifuged and the supernatant was counted to determine the fraction of Pu(V+VI). By comparing the fraction of Pu(IV) from the LaF_3 coprecipitation against the liquid-liquid extraction, one could confirm the success of the oxidation analysis. An experimental error from this method was stated to be ± 5% giving reasonable confidence of the distribution of oxidation states.

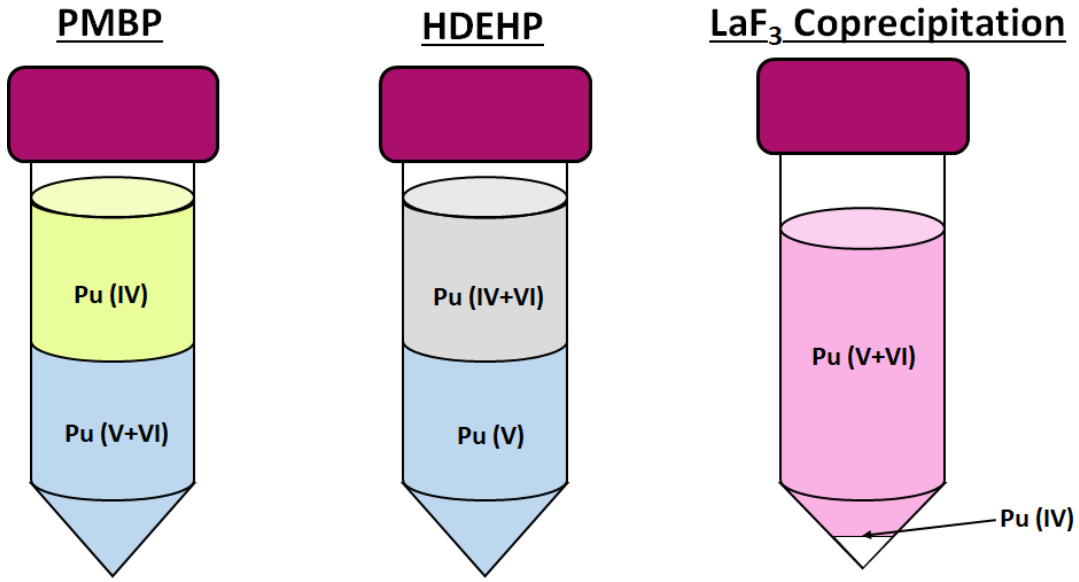

Figure 12: *Conceptual design to determine Pu oxidation state.*

4.2.3 DBM extraction chromatography resin

The DBM extraction chromatography resin was made through a series of steps where the DBM ligand was dissolved in an organic solvent and impregnated within an inert resin bead. The 120 µm resin bead (Amberchrom CG-300C Tosoh Corporation) was composed of polystyrene and divinylbenzene polymer. The resin was mixed with 0.2 M DBM in 1-octanol and methanol for 24 hours. This was to ensure the ligand was penetrating the resin. The ratio of organic, not including methanol, to resin mass was 0.4.

After 24 hours, the mixture was subjected to 40°C and a vacuum and mixed until all methanol had been evaporated allowing free flow of beads in a rotary vacuum. This resulted in the methanol evaporating leaving the DBM-extraction chromatography (DBM-EC) resin behind. In addition to the DBM-EC resin, a control resin, octanol-only-extraction chromatography (O-EC) resin, was made with 1-octanol that had no ligand.

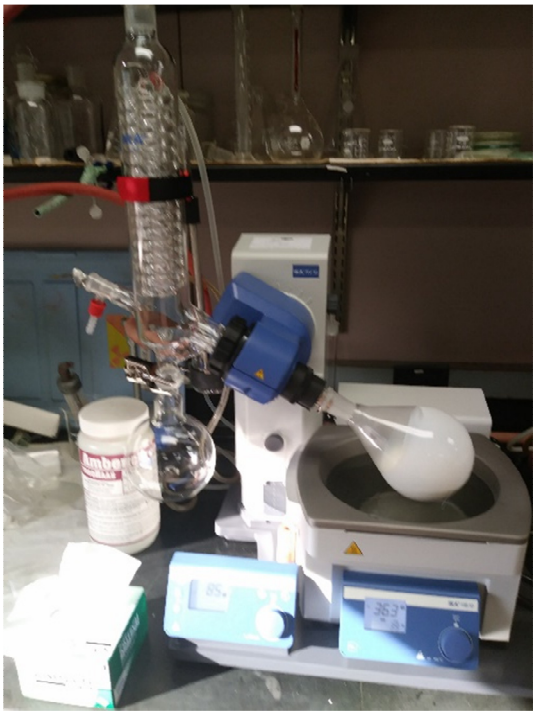

Figure 13: *IKA RV 10 Rotary evaporator used for creation of extraction chromatography resin.*

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Analig® Pu02 Modification

5.1.1 Initial uptake and radioluminosity characterization

The first modification of the Analig®Pu02 (MA) resin was characterized by a batch uptake and off-line detection experiment. Approximately 10 mg of the MA resin was mixed with 3 mL of a pH 1 ^{242}Pu solution (6 Bq/mL) and mixed for three hours. The MA resin was successful for Pu uptake (>99%); however, expressed poor radioluminosity ($\varepsilon_d \approx 2\%$). It was hypothesized that the lack of luminosity was due to low organic scintillator mass on the bead as a result of high binding capacity, i.e., the degree saturation of organic ligands incorporated onto the resin. Therefore, the lack of exposed silica sites likely hindered silanization process, preventing attachment of the scintillator components. It was hypothesized that to overcome the minimal sites for the scintillator, the Analig® Pu02 resins were subjected to grinding and crushing with a mortar and pestle. Here, the cleaved and exposed silica sites would increase likelihood of a successful silanization of the resin surface, in turn increasing attachment and growth of organic scintillating polymer (**Figure 14**).

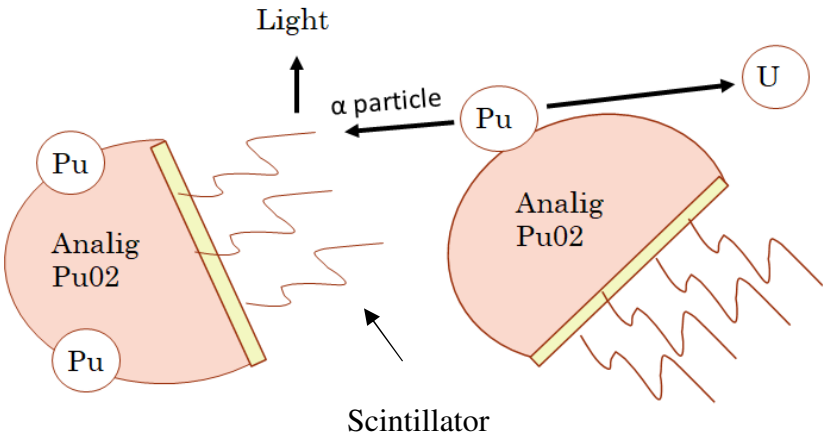

Figure 14: *Hypothesis that exposing silica sites by grinding and crushing would increase detection efficiency.*

The influence of crushing the Analig® Pu02 resins prior to modification was investigated with a series of ^{242}Pu uptake batch experiments at various steps of the modification process. ε_u for ^{242}Pu (30 Bq/mL) was determined with a pH 1 solution for 3 hour contact time (**Table 2**). Overall uptake was high for all resin samples indicating that the modification process resulted in a notable, but insignificant impact on performance. The crushed unmodified Analig® Pu02 (CA) resin had approximately the same uptake as the Raw Analig® Pu02 resin; however, the uptake decreased for the silanized Analig® Pu02 (SA) resin from >99% to 93% uptake. This indicates that the introduction of the MPS may have chemically altered the ligand sites and thus decreasing uptake performance slightly. The crushed and modified Analig® Pu02 resin (CMA1), had the lowest uptake of 89% which is was not unexpected because complexation sites previously available for Pu uptake were likely disturbed by nearby scintillation attachment and chemical alteration occurring from the modification procedure. Although

the ^{242}Pu uptake decreased with modification, the uptake was still high at approximately 90% indicating a successful first product.

***Table 2**: Initial uptake results for the two modified Analig®Pu02 resins at pH 1 with 3-hour mix.*

Sample at pH 1	**K_d (mL/g)**	**ε_u (%)**
Raw Analig® Pu02	11798	>99
Crushed Analig®Pu02 (CA)	21273	>99
Silanized Analig®Pu02 (SA)	2670	93
Crushed Modified Analig®Pu02 (CMA1)	1781	89

The crushed and modified Analig®Pu02 (CMA1) resin was further characterized with a series of off-line radioluminosity measurements. The CMA1 and CA resins were subjected to batch loading of aqueous 14 Bq/mL of ^{242}Pu at pH 1 for 24 hours. The two Pu-loaded resins were then inserted into a PFA column tube, dried, and counted by LSC to generate counts and spectra (**Figure 15**). The presence of ^{242}Pu resulted in a clear peak for the CMA1 resin, while no distinguishable peak was present for the CA resin. These results indicated scintillation light was produced solely from the ^{242}Pu interacting with the modified resin. Here, the alpha particles emitted from the decay of Pu were in range to interact with the scintillating material and produce measurable light. The detection efficiency (ε_d) for this procedure was determined to be 36.5% which was considered to be an adequate value to further investigate the Analig modification procedure and formulation.

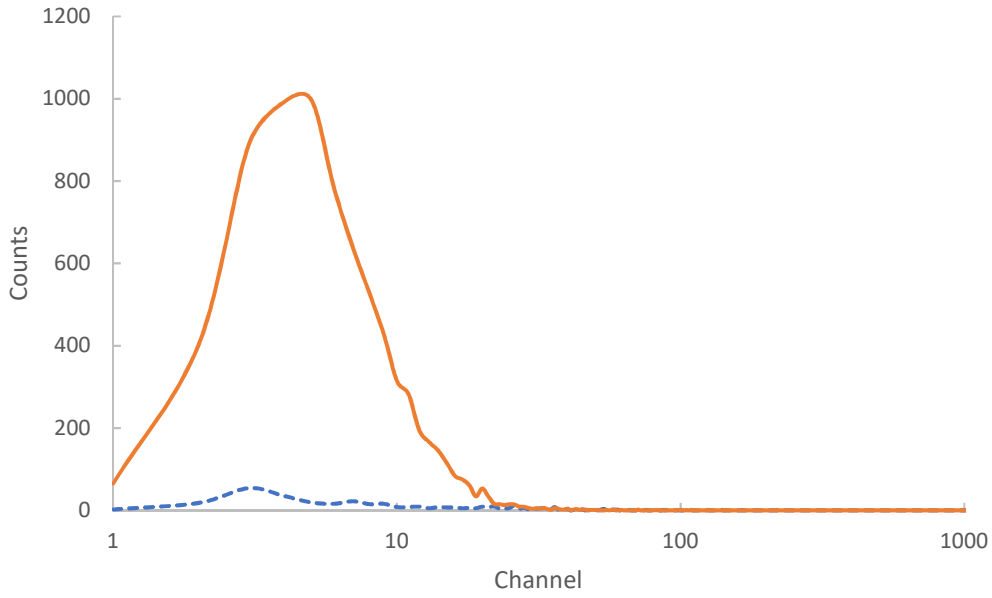

Figure 15: *Luminosity spectrum for an off-line experiment where the modified crushed Analig®Pu02 (CMA1) resin (solid-orange) and the crushed unmodified Analig®Pu02 (CA) resin(dotted-blue) were in contact with a 14 Bq/mL ^{242}Pu solution. The samples were counted for 15 minutes.*

5.1.2 Reproducibility

The resin modification was repeated to confirm reproducibly and generate more resin for further studies. The new resin, CMA2, was made the same way as the first modified resin (CMA1) and was subjected to initial characterization of uptake and radioluminosity. Here, 10 mg of CMA2 was mixed with a pH 1 solution of ^{242}Pu (12 Bq/mL) for approximately three hours. The supernatant was counted and the resin beads were inserted into a plastic column and counted by LSC. The performance of CMA2 was unexpectedly poor, with both uptake efficiency and detection efficiency at 41.5±0.3% and 10.8±0.1%, respectively (**Table 3**). To develop a better understanding of the differences between CMA1 and CMA2, three additional resins were produced (CMA3-CMA5) and

examined for uptake and radioluminosity. Of all the new resins, CMA3 performed the best but still had lower detection efficiency than CMA1 (**Table 3**). It was hypothesized that there could be a correlation between detection and uptake efficiency however no such correlation existed when further examined. The difference in uptake and detection efficiency is likely due to the modification procedure and experimentation methods. The uptake experiments were performed separately and slight alterations in procedure methods may have influenced uptake and detection efficiency. For example, ^{242}Pu solutions may have had slight pH differences or shaking times that could have had cumulative effects influencing uptake or detection. Performing procedures simultaneously with the resins would have provided a more comprehensive understanding of performance. This was unable to occur due to low resin mass, aging of resins, and unforeseen variability in resin performance. Resin modification procedures are likely the primary source of variability with performance and are thoroughly discussed below in **Section 5.1.3**.

Table 3*: Summary of modified Analig® resins that were modified in the same way. Approximately 10 mg of resin were shaken with 3mL of ^{242}Pu for 3 hours with resin and supernatant being counted by LSC. Error is due to counting statistics.*

CMA #	ε_u (%)	ε_d (%)	ε_t (%)
1	89.0 ± 2.6	36.5 ± 0.2	32.5 ± 1.0
2	41.5 ± 0.3	10.8 ± 0.1	4.5 ± 0.1
3	95.3 ± 4.6	15.6 ± 1.1	14.9 ± 1.3
4	97.5 ± 5.9	3.8 ± 1.6	3.7 ± 1.6
5	62.5 ± 0.5	8.4 ± 0.1	5.3 ± 0.1

5.1.3 Investigation of modification parameters

Due to the variability of uptake and detection efficiency with the modified resins, several parameters in the modification process were further examined. These parameters consisted of: time of silanization (step 1), time of polymerization (step 2), and particle size (**Table 4**). Additionally, some of the modifications were changed to reflect previous experiments more accurately (Seliman et al., 2017; Wang, et al., 2009). The changes consisted of (a) performing the silanization in a closed atmosphere where the mixture was sparged with nitrogen gas and (b) washing the finished polymerized with ethanol and water only. Additionally, a magnetic stir bar was utilized rather than the overhead IKA® RW 11 mechanical stirrer. This was done as the low torque of the stirrer resulted in sporadic failure to mix.

Table 4: *Summary of varying modification time and particle size. The efficiency values were determined using ^{238}Pu solution and 3 hours shaking time with 10 mg of resin.*

Silanization Time (hr)	Polymerization time (hr)	Particle Size (μm)	ε_u (%)	ε_d (%)	ε_t (%)
6	12	<63	34.9 ± 0.6	23.2 ± 0.7	8.1 ± 0.3
		63-106	39.5 ± 0.7	19.7 ± 0.6	7.8 ± 0.3
		106-180	33.5 ± 0.6	15.4 ± 0.6	5.2 ± 0.2
	24	<63	45.7 ± 0.8	13.0 ± 0.4	5.9 ± 0.2
		63-106	48.7 ± 0.9	10.3 ± 0.4	5.0 ± 0.2
		106-180	43.8 ± 0.8	10.3 ± 0.4	4.5 ± 0.2
12	12	<63	43.4 ± 0.7	15.5 ± 0.5	6.7 ± 0.2
		63-106	39.3 ± 0.7	13.7 ± 0.5	5.4 ± 0.2
		106-180	36.1 ± 0.6	15.5 ± 0.5	5.6 ± 0.2
	24	<63	41.0 ± 0.7	15.1 ± 0.5	6.2 ± 0.2
		63-106	45.9 ± 0.8	10.4 ± 0.4	4.8 ± 0.2
		106-180	42.7 ± 0.8	8.1 ± 0.3	3.5 ± 0.2

Uptake efficiency was determined for the varying modifications of the Analig® Pu02 resins with a 12 Bq/mL ^{238}Pu solution. (**Figure 16**). Samples were shaken for three hours at pH 1. Uptake was relatively constant among the resins at approximately 40% with small discrepancies. It appeared that the 63-106 μm beads had the highest of Pu uptake, however the uptake of the various sizes were mostly within error. The CMA-6S12P resin had the lowest uptake efficiency at 34±1% for the 106-180μm resin. The poor uptake of the CMA-6S12P resin was interesting as this was the same modification that resulted in the highest detection efficiency (**Figure 17**). It is likely that the successful attachment of scintillator decreased likelihood that the Pu atom could migrate through the scintillator during mixing and be extracted by the proprietary ligand on the surface of the resin.

The low ^{238}Pu uptake was unexpected, as previous experiments had resulted in >90% Pu extraction. However, those experiments were performed with a ^{242}Pu solution with majority Pu(IV) solution. The ^{238}Pu solution used in the uptake experiment (**Figure 16**) had a Pu distribution of approximately 28±5% Pu(IV), 24±5% Pu(V), 49±5% Pu(VI). It is likely, that all of the Pu(IV) and some Pu(V) was extracted. This can be attributed to previous experiments where an unmodified Analig® Pu02 resin achieved approximately 80% Pu(V) uptake within one hour of contact (Appendix A). This is likely due to surface mediated reduction of Pu(V) to Pu(IV). To examine the low uptake, the CMA-12S24P (<63μm) sample was immersed with a new ^{242}Pu solution with 58±5% Pu(IV) and 42±5% Pu(V) in a batch reactor. After shaking for three hours, uptake was approximately 96% indicating that most of the Pu(V) was extracted. This likely indicated that discrepancy in

uptake with the ^{238}Pu and ^{242}Pu can be attributed to Pu(VI) not being extracted and the molar concentrations of the two isotopes.

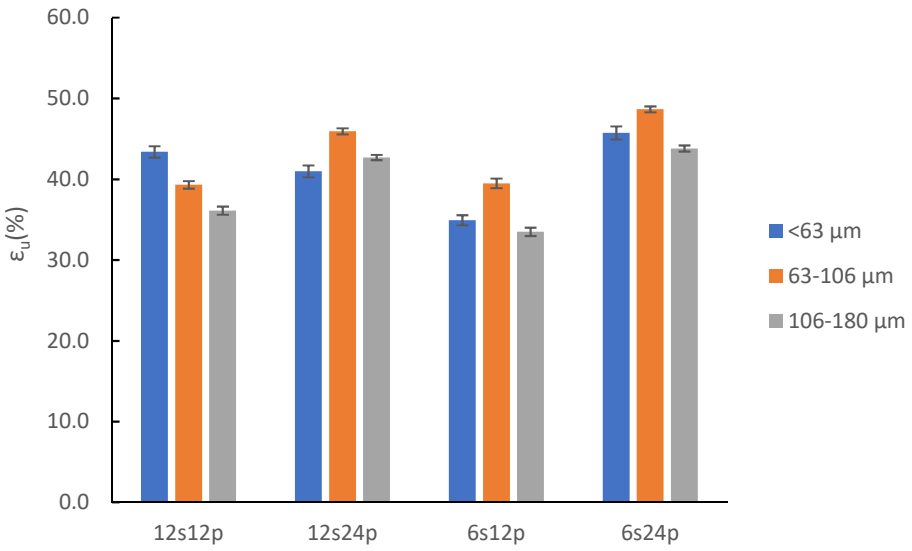

***Figure 16**: Total ^{238}Pu uptake efficiency (ε_u) of modified Analig® samples based off of silanization time (s) and polymerization time (p). Samples were mixed for 3 hours at pH 1. Error bars represent 1σ counting statistics.*

The detection efficiency for each modified resin was examined by an off-line measurement and counted via LSC (**Figure 17**). The resins with 6 hours silanization and 12 hours polymerization (CMA-6S12P) appeared to have the highest detection efficiency with 23±1%. This was also higher than CMA2-CMA5 which had 12 hours of silanization and 24 hours of polymerization(12S24P). Generally, the detection efficiency decreased as particle size increased. This was especially apparent in the CMA-6S12P sample. This is most likely due to short range of the alpha particle and the increased ratio of scintillator to ligand sites in smaller resin beads. The poorest detection efficiency was observed in the 24hr polymerization samples (24P), particularly with the largest size beads (106-180µm). This is surprising, as longer polymerization time should theoretically increase the likelihood of energy deposition of the alpha particle into the

larger amount of scintillator. It is possible that the long modifications times could result in degradation of the resin or attenuation of light. This could explain how the CMA-6S12P resins, samples having the least amount of modification time, had the highest detection efficiency.

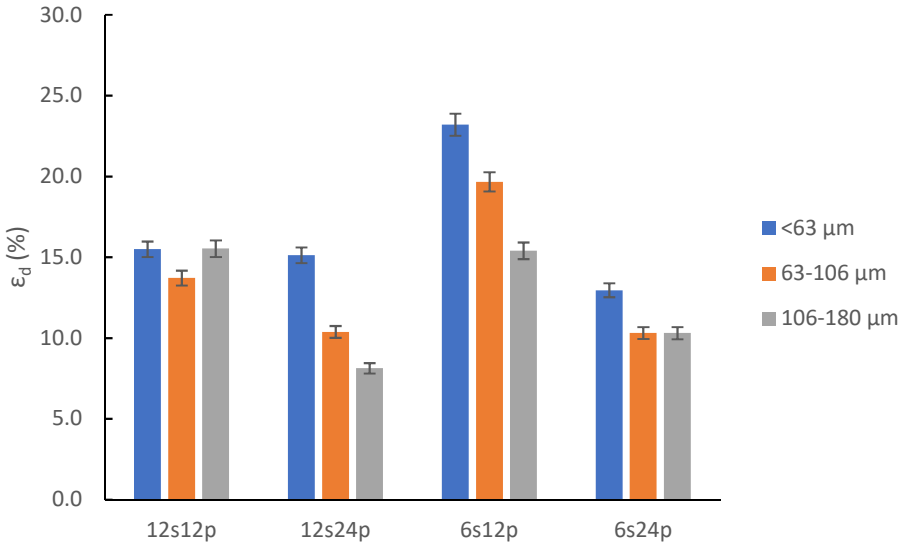

Figure 17: *Detection Efficiency (ε_d) of modified Analig® samples based off of silanization time (s) and polymerization time (p). Error bars represent 1σ counting statistics.*

The total efficiency was determined from the detection and uptake efficiencies (**Figure 18**). The highest efficiency was with <63µm CMA-6S12P sample at 8±0.3%, indicating that the shortest modification is likely the overall best option for future resin modifications. In fact, all resins of size <63µm had the higher efficiencies than the larger resin sizes. It should be noted though, that smaller particle size could have an influence if column flow conditions were applied and results in restriction of flow and large pressure buildups.

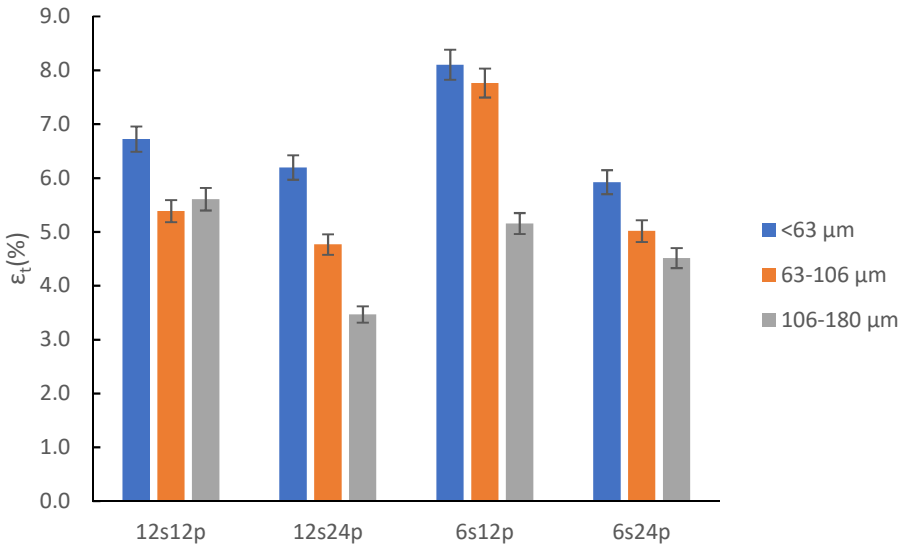

***Figure 18**: Total efficiency (ε_t) for ^{238}Pu and modified Analig® samples based off of silanization time (s) and polymerization time (p). Error bars represent 1σ counting statistics.*

One important factor that became apparent when conducting the modification experiment, was the change in particle size due to modification (**Figure 19**). After each modification step, the resin was sieved and the mass fractions were counted. A trend was observed showing a shift from large particle size to small particle size through the modification process. This was likely due to chemical-induced degradation and/or physical abrasion from the modification procedure and the addition of the magnetic stir bar. After the initial crushing of the Analig® Pu02, there was no amount of resin that was associated with the <63µm fraction and most of the resin was in approximately a 1:1 relationship of 63-106 µm and 106-180 µm sizes. As the modification progressed, the <63 µm resin fraction grew to become the largest size fraction after polymerization, leaving little 106-180 µm resin remaining. It is fortunate that the smaller resin sizes had increased efficiency; however, it should be noted that the chemical and physical

modification procedure utilized in this experiment resulted in a particle size decrease with increased processing.

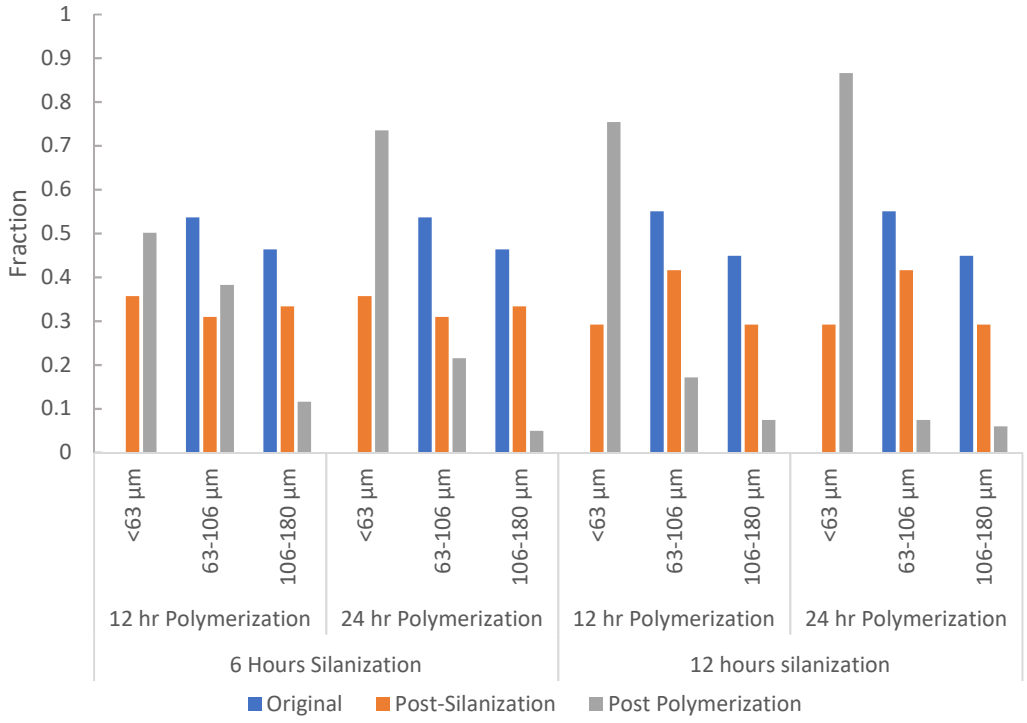

Figure 19: *Summary of particle size fractions throughout the modification procedure.*

5.1.4 Confocal microscopy of modified Analig® Pu02 resins

Confocal microscopy was utilized to determine spatial distribution of the vNPO fluor attached to the Analig® Pu02 resins. The modified resins consisted of three size distributions of CMA-6S12P resins and an uncrushed-modified (UMA) resin sample. A Raw Analig® Pu02 resin was examined as well. All resin particles appeared irregular in shape (**Figure 20**). No emission of light was detected with the Raw Analig® Pu02 resin when exposed to the laser. This was expected as no surface modification had been

performed. The laser-induced fluorescence of the UMA resin indicated no evidence showing that scintillating polymer was attached in any degree to the uncrushed Analig® Pu02 resin; however, there were several pockets with low light intensity that were difficult to observe (**Appendix E**). The trace amount of light was likely due to the surface modification process where some pockets originally had exposed silica or dust within the sample tray. This helped support the hypothesis that mechanically cleaving and crushing the resin prior to modification aids in the attachment of scintillating polymer that could improve radioluminosity.

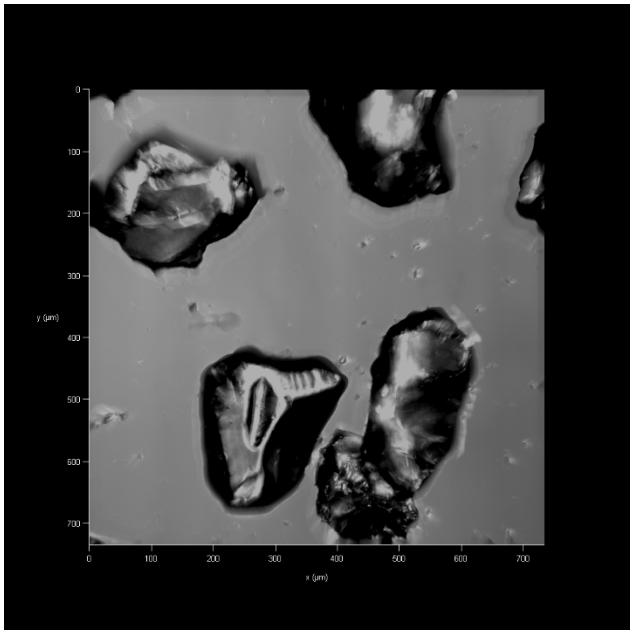

Figure 20: *Confocal micrograph of Raw Analig Pu02 resin viewed with confocal microscope (no laser in image). The silica beads are large and irregular shaped. No emission of light when exposed to laser (not shown).*

The CMA-6S12P resin of <63µm, 63-106 µm, and 106-180 µm sizes was examined with confocal microscopy. It was selected because it was had the highest detections efficiency of the respective resins. The larger 106-180µm resins expressed both large heterogeneous pockets of fluorescence along resin edges and areas void of

fluorescence in the bulk resin (Not Shown). The pockets of bright fluorescence appeared to form largely from cleaved sites where crushing occurred. The 63-106 μm (**Figure 21**) and <63μm resins appeared to show similar behavior, but to a lesser degree. As resin size decreased, the distribution of fluor appeared to be more uniform. This was expected as the ratio of cleaved sites to ligand sites increased as particle size decreased. Sectional slices were taken for the CMA-6S12P resin samples and indicated that majority of fluor is attached to the surface and not within the interior of the resin bead.

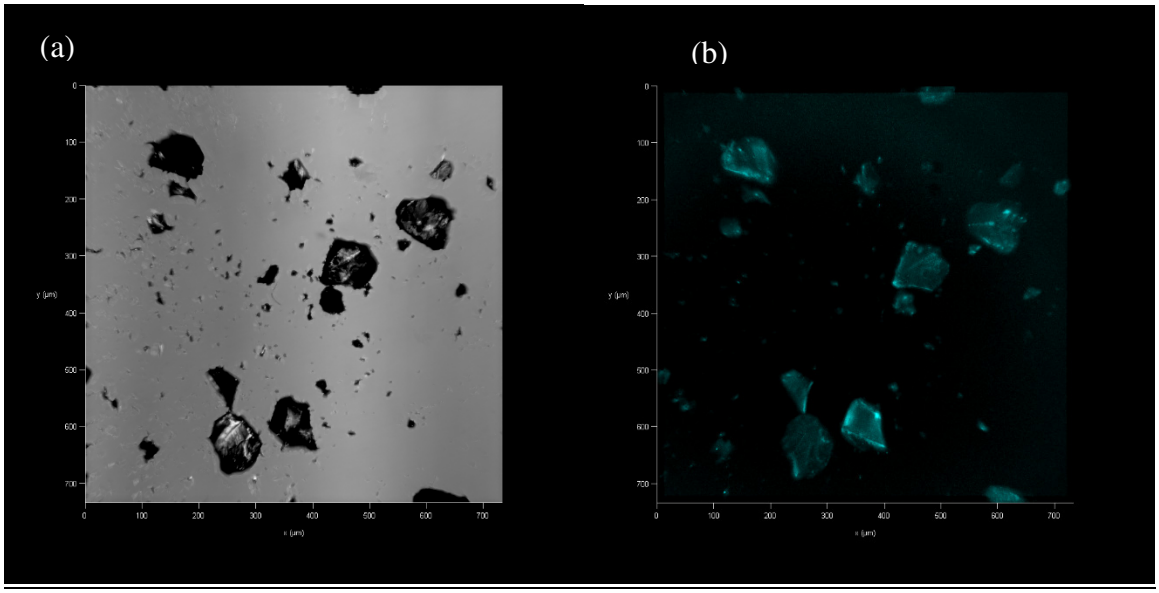

Figure 21: *Confocal micrograph images of CMA-6S12P resin of 63-106μm. (a) Light image with no laser. (b) fluorescence (cyan color) of fluor due to laser.*

5.1.5 Column size and material influences

Investigation of effects on column size and material composition on detection efficiency were carried out using CMA1 resin (**Table 5**). Approximately 20 mg of

CMA1 resin was exposed for 19 hours with a ^{238}Pu (3 Bq/mL) solution at pH 2. The supernatant Pu was counted on LSC and the loaded-resin mass was recorded and inserted into the 5-cm plastic columns. The columns were placed in the LSC overnight for dark adaption and counted the following day. This detection efficiencies observed in this experiment were substantially higher than from the initial uptake experiment where detection efficiency near 36% ^{242}Pu(IV) uptake. This could be due to Pu diffusion in the resin, chemical equilibrium or possibly be related to decay energies. The alpha particle energies from ^{238}Pu are higher compared to ^{242}Pu and could travel approximately 5 μm further in water increasing likelihood of interaction with scintillator. Performing the experiment in triplicate would likely reflect a more accurate answer. Unfortunately, there was not enough CMA1 resin material to repeat the experiment to investigate the discrepancies in detection efficiencies of the two experiments. The detection efficiencies were consistent among the three columns at 54 to 58% ^{238}Pu(IV+V) even when the columns appeared to have irregular packing and distribution along the column length (**Figure 22**). Overall, the material and column size indicate little influence with detection efficiency for the CMA1 resin in these experimental conditions.

***Table 5**: Summary of the plastic type and column size with the associated detection efficiency for ^{238}Pu.*

Tube	Inner Diameter	Outer Diameter	Material	ε_d
A	1/16”	1/8”	PFA	0.58
B	1/8”	3/16”	FEP	0.58
C	1/8”	1/4”	PTFE	0.54

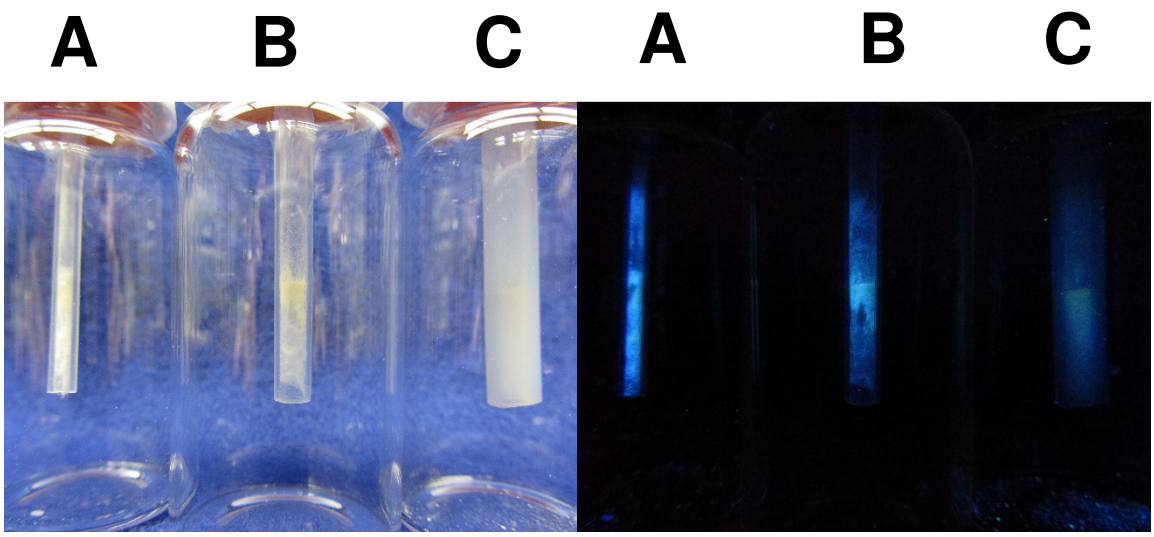

Figure 22: *The first photograph shows the loaded columns positioned in a 20mL glass LSC vial. The next photograph demonstrates the uv fluorescence of the scintillator in the resin.*

5.1.6 Environmental Influences on Resin Performance

The performance of the modified Analig® Pu02 with potentially relevant environmental competitors was investigated. It was important to consider the many factors that needed to be considered for real world applications due to the complexity of environmental matrices. Only four particular ions were selected to examine competition with Pu due to constraints on resin mass and time. Calcium (Ca(II)) was chosen as it commonly found in natural waters (Langmuir, 1997) and would provide information of incorporation of divalent cations with the modified Analig® Pu02. Iron (Fe(III)) was considered next because Analig® Pu02 is known to have high affinity for Fe(III) (Dulanská et al., 2011). Other environmental relevant actinides were examined, due to the potential to contribute to counts and provide false Pu measurements. These actinides are ^{238}U and ^{232}Th which are natural sources of radioactivity in many groundwaters (Langmuir, 1997). The solutions were adjusted to different concentrations to examine competition with Pu on a molar basis. The ^{242}Pu concentration used was approximately

10^{-6} M (≈ 20 Bq/mL, pH 1) and all four potential competitors were evaluated at 10^{-6} M to observe a 1:1 molar competition. Additionally, other environmental relevant concentrations were investigated. The concentrations and nomenclature are listed in **Table 6**. A batch uptake experiment examining ^{242}Pu competition with the environmental constituents was performed (**Figure 23**).

Table 6: *A summary of potential competitor concentrations. These competitors were used to examine competition with ^{242}Pu for modified Analig® Pu02. The ^{242}Pu concentration was 10^{-6}M* (Davis & Dewiest, 1966; Rose, et al., 1979; Turekian, 1977).

Constituent		Concentration (M)	Notes
Ca(II)	Low	1.00E-06	1:1 with ^{242}Pu
	Med	1.00E-03	Groundwater concentration
	High	1.00E-02	Average seawater concentration
Fe(III)	Low	1.00E-09	Lower limit of groundwater concentration
	Med	1.00E-06	1:1 with ^{242}Pu
	High	1.00E-03	Upper limit average groundwater concentration
^{238}U	Low	1.00E-09	Median groundwater concentration
	High	1.00E-06	1:1 with ^{242}Pu
^{232}Th	Low	1.00E-09	Median groundwater concentration
	High	1.00E-06	1:1 with ^{242}Pu

Using the standard batch uptake experiment, approximately 10 mg of CMA3 resin was contacted with a ^{242}Pu solution for three hours. The resin was centrifuged and the supernatant was counted by LSC. High uptake (>85%) was observed in all samples except for the Fe-High sample (10^{-3} M Fe(III)) at approximately 60%. The low uptake of Pu in the higher Fe(III) sample indicated that high Fe(III) samples are likely to interfere with Pu uptake and proper considerations should be applied in these types of environments. It was suspected that the other ions would partially interfere with Pu uptake but it was shown that there was no effect on Pu uptake with the modified Analig®

Pu02 resin. The lack of calcium (II) competition could indicate that the modified Analig® Pu02 could be used in salt water matrices. The little influence of ^{238}U and ^{232}Th indicates that these natural radioactive actinides would likely not contribute to false Pu readings in most environmental samples even when at elevated concentrations.

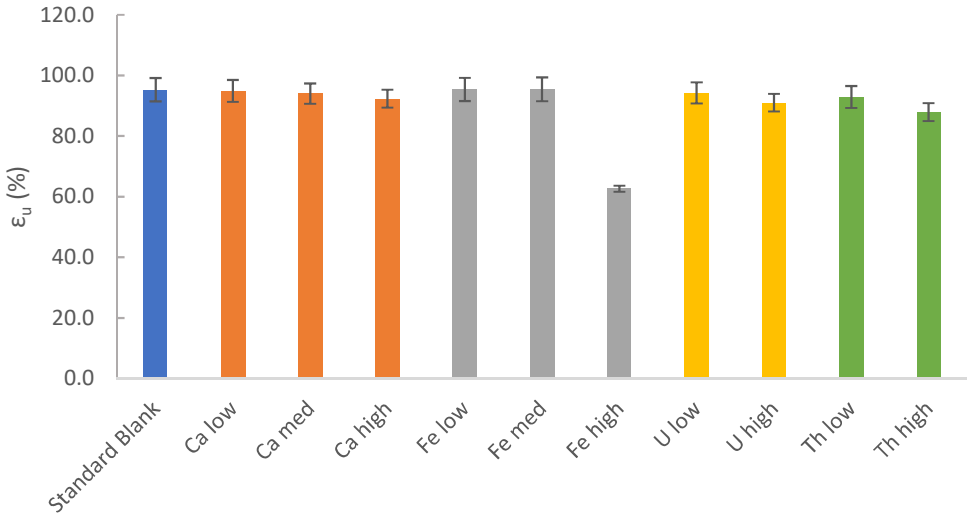

***Figure 23**: Uptake of ^{242}Pu when paired with varying concentration of groundwater constituents for a pH 1 solution. Error is due to counting statistics.*

5.1.7 On-Line detection with modified Analig® Pu02

Further experimentation investigated the use of the modified resin for detection in real time using a flow cell with photomultiplier tubes (Beta-Ram, LabLogic). It was of interest do determine how the uptake and detection efficiencies would differ with respect to batch experiments. **Figure 24** is an example of the typical conditioning and loading of a column in an on-line experiment. The first loading consisted of conditioning the column, containing 43.7 mg of CMA1, with 10 mL of 0.1 M HNO_3. Next, the column was loaded with 10 mL of 12.6 Bq/mL of majority $^{242}Pu(IV)$ with 0.1 M HNO_3. After the loading of ^{242}Pu, another 10 mL of the conditioning solution was applied to stabilize a

plateau count rate. The column was then subjected to an eluent consisting of 0.5 M citric acid to determine if it would remove the bound ^{242}Pu. The flow rate approximately 0.3 mL/min in all cases. The eluent was unsuccessful at removing Pu; in addition, a chemical luminescence reaction occurred among the modified resin and the citric acid (not shown) causing a spike in count rate unrelated to radioluminescence. Effluent activities were later analyzed after each step to quantify efficiencies. The uptake and detection efficiency were 71.5% and 28.5%, respectively and resulted in a total detection efficiency of 20.4%.

An additional on-line experiment was tested using 34 mg of CMA3 resin with 59±5% ^{242}Pu(IV) and 47±5% ^{242}Pu(V) (**Figure 25**). The loading scheme was the same as the CMA1 resin, however flow rate was approximately 0.6 mL/min and supplied by an external pump due to pressure buildup. The uptake and detection efficiency for CMA3 were 97.0% and 8.3%, respectively. The difference in uptake was not expected, as it would be expected that slower flow rate would result in increased uptake. This was not observed, however, as the CMA3 resin had much higher uptake when compared to the CMA1 resin. The ^{242}Pu solution used in the on-line measurement of CMA3 contained more Pu(V) in solution than the CMA1 indicating that oxidation state was not solely influencing uptake. It is likely that that differences in uptake between the two resins could be attributed to the much smaller CMA3 resin particles that required the utilization of an external pump to allow for flow. This would allow for more surface area per unit travel-distance within the cell that could have resulted in the enhanced uptake for CMA3. More trials with on-line measurements with the same exact flow set-up and solutions

could provide more insight into discrepancies of uptake efficiencies Detection efficiency values were more consistent than uptake efficiency. Both CMA3 and CMA1 decreased by approximately 8% when compared to their respective off-line measurements. This is likely due to the water saturating the pore space and decreasing interactions of alpha particles and scintillator.

Both on-line measurements expressed a consistent slope from the loading of Pu. This indicates that resin had plenty capacity and that resin saturation was not achieved. If saturation was achieved, breakthrough would occur and the loading slope would decrease appearing non-linear. It is likely that Pu distribution along the resin column was not uniform, and that there would be a higher concentration of Pu at the inlet. This is not a concern, however, because the slope response appeared immediately once the Pu was introduced. This indicates that position of Pu distribution along the resin column does not significantly affect detection performance as long as all resin is within the windows. Longer loading periods would substantiate the effects of loading distribution on detection efficiency. Overall, the on-line detection method proved that commercial extractants were able to be modified and obtain real time activity of plutonium solution activity.

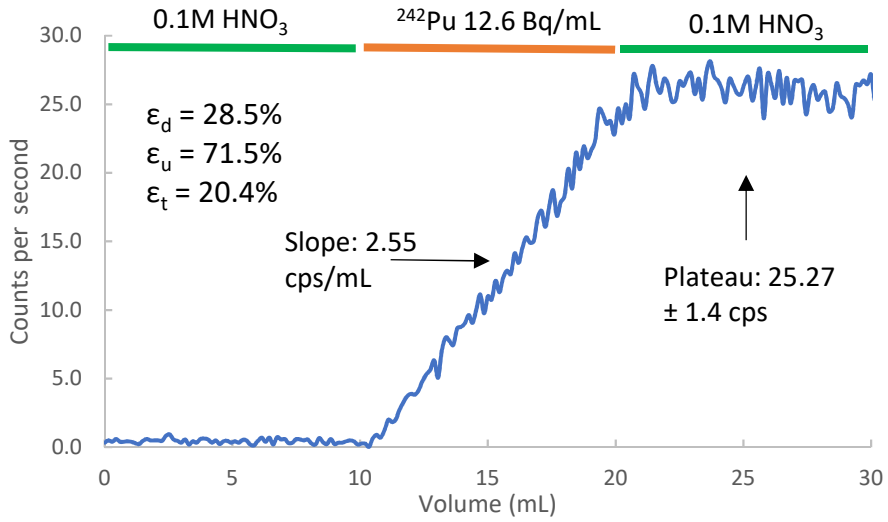

***Figure 24**: On-line measurement of loading a majority ^{242}Pu(IV) in 0.1 M HNO_3 using CMA1 and Beta-Ram.*

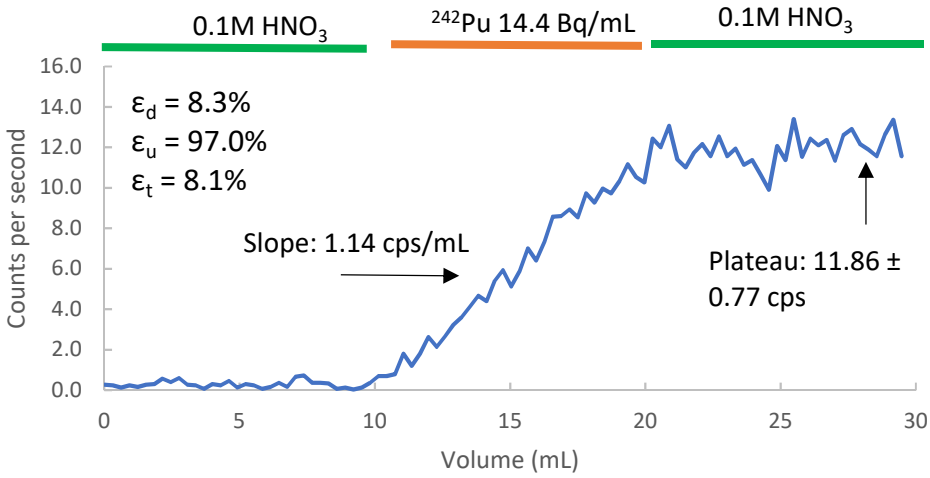

***Figure 25:** On-line measurement of loading ^{242}Pu with 0.1 M HNO_3 using CMA3 and Beta-Ram. Pu(IV)and Pu(V) distribution were 59±5% and 47±5%, respectively.*

5.1.8 Minimum Detectable Concentration for modified Analig® Pu02 resin

The minimum detectable concentration (MDC) was determined for the CMA1 resin using the previously mentioned off-line and on-line experiments. The MDC (Bq/L)

was calculated using **Equation 6** with inputs provided in **Table 7**. The MDC values for the off-line and on-line experiments were 45.6 and 34.9 Bq/L, respectively. These values were two orders of magnitude higher than the 0.56 Bq/L MCL for gross alpha activity in drinking water (EPA, 2000). The MDC values for both measurements could be decreased through manipulation of some key variables. The simplest approach to achieve lower MCL concentrations would be to increase both volume and count time; however, attempts to reduce MDC solely through high counting times would have diminishing effects due to the square root in **Equation 6**. Therefore, a counting time should be selected that optimizes both sample processing and counting. After selection of counting time, attempts should be made to increase solution volume to achieve a decreased MCL. For example, increasing volume from 4 mL to 330 mL would achieve a MDC value of 0.56 Bq/L using the off-line parameters provided in **Table 7.** Another parameter that is more difficult to modify, but could still provide a decreased MDC is ε_t. One could enhance ε_t for the system by establishing longer contact time and altering the solution chemistry to increase Pu extraction. The is because ε_t is the product of both uptake and detection efficiency. Parameters like the detection efficiency and background count rates are likely to remain fixed unless a new resin and detections systems are implemented.

The on-line system provided challenges when utilizing **Equation 6** and several assumptions were made that could have resulted in a high MDC value of 34.9 Bq/L. The explanation on how the parameters were applied in **Equation 6** are further described. For example, the counting of loaded sample and background both occurred for 33 minutes (10 ml of flow) and appeared as the first and second “plateau” in **Figure 24**. The

counting occurred during flow of solution through the column and by averaging count rate over the 33-minute count time. The averaging of count rates was due to the limitations of a 30-second maximum dwell time for the Beta-Ram instrument and accompanying software. A more accurate and applicable model would allow column loading with larger volumes followed by stoppage of flow with subsequent count time. Work by Grate et al., 2008 utilized this on-line approach for ^{99}Tc in groundwater with a scintillating extraction chromatography resin. They were able to achieve MDC values of 6 Bq/L with count times of 30 minutes after each loading of 50 mL of groundwater indicating that efforts can be improved to decrease MDC values in a flow-cell experiment.

***Table 7**: Summary of inputs applied to determine MDC (Bq/L) for off-line and on-line experiments with CMA1 resin.*

Sample	Background Count Rate, C_b (cps)	Total Efficiency, ε_t	Count Time (s)	Volume (mL)	MDC (Bq/L)
CMA1 off-line	0.13	0.32	900	4	45.6
CMA1 on-line	0.45	0.20	2000	10	34.9

5.2 DBM Resin

5.2.1 Liquid-liquid extraction test

Several preliminary studies were performed with DBM to investigate the feasibility of incorporating the ligand into a DBM-Extraction Chromatography (EC) resin. The first study investigated choice of solvents for DBM. Low boiling point solvents such as benzene were previously used for DBM extraction procedures (Kobashi et al., 1993; Saito & Choppin, 1983). EC resins utilize solvents with high boiling points to prevent evaporation during the resin creation process. High boiling point solvents were investigated to replace benzene as a solvent.

Toluene and 1-octanol were the initial candidates tested at a DBM concentration of 0.2 M. The DBM instantly dissolved in the toluene, but took longer to dissolve in the 1-octanol. The 0.2 M DBM in 1-octanol was the highest concentration that would could be prepared. No solubility test was performed with toluene, but it would be expected to maintain higher DBM concentrations as it is less polar. The initial uptake procedure included 0.5 mL of a ^{242}Pu (3 Bq/mL) phase at pH 6 and 0.5 mL of the organic phase that were shaken for approximately one day (**Figure 26**). The activities were compared against the initial activity before mixing. An oxidation analysis (OA) was performed on the original ^{242}Pu stock solution in 0.3M HNO_3 indicating 53±5% Pu(IV) and 47±5% Pu(V). No oxidation state analysis was performed following pH adjustment up to pH 6, but it would be expected that the Pu(IV) concentration would decrease with increase in pH due to oxidation to Pu(V) and loss to solution due to wall sorption, precipitation, and

hydrolysis. In later experiments, the discrepancy in Pu speciation with pH is addressed and Pu oxidation analyses are tested more rigorously.

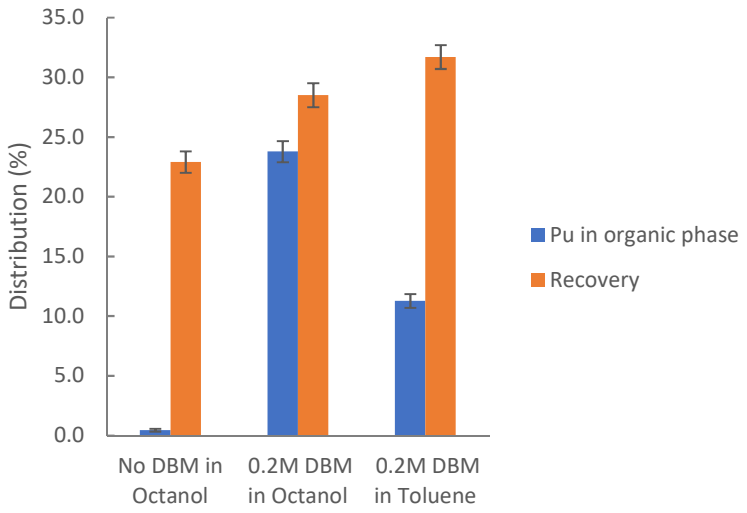

***Figure 26**: Initial liquid-liquid extraction examining uptake of 3 Bq/mL ^{242}Pu at pH 6 when shaken for 1 day. Error bars are due to counting statistics.*

Total Pu uptake into the organic phase for the 1-octanol and toluene DBM samples were relatively low at approximately 24% and 11%, respectively. The preferential uptake in 1-octanol is likely due to the Pu-DBM complex preferring a more polar solvent such as 1-octanol. There was no uptake in the organic phase without the presence of DBM indicating that DBM was indeed influencing Pu uptake. Plutonium-242 recoveries were also poor indicating that Pu was being removed from solution most likely due to wall sorption or precipitation as a Pu(IV) species at neutral pH.

5.2.2 Influence of pH and Pu speciation with DBM uptake

Several parameters were analyzed to gather an overall impression on the interaction of 0.2 M DBM in 1-octanol and Pu. The next step was to examine the

influence of pH as it is often one of the master variables for extraction. The hydrogen ion concentration influences Pu speciation, surface charges, and oxidation states. It is recommended the Pu extraction procedures for Pu(IV) and DBM should occur at a pH of 4 to 5 (Saito & Choppin, 1983). A liquid-liquid extraction using a ^{238}Pu (3 Bq/mL) solution with 66±5% Pu(IV) was tested from pH 2.3 to 5.5 (**Figure 27**). Testing at a higher pH was shown from previous experiments to start having significant complication with Pu recovery. Even increasing pH from 2.3 to 5.5 resulted in a decrease in Pu(IV) species distribution. Acetate was added to the aqueous solutions at 0.01M to inhibit wall sorption and help with pH buffering during titration. Each vial had 0.6 mL of each phase and was shaken for five minutes. The 5-minute contact time was later shown to be unfavorable and that longer contact times should be attempted in future experiments.

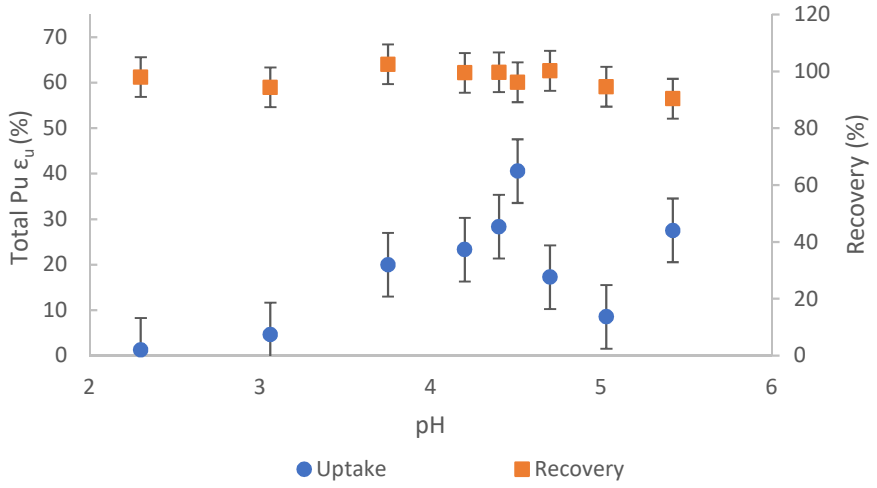

Figure 27: *Summary of liquid-liquid extraction with 0.2 M DBM in 1-octanol where pH and uptake efficiency for total ^{238}Pu (3 Bq/mL) are examined. The initial stock is 66% Pu(IV). All samples were shaken for 5 minutes. An error of 7% is applied to all liquid to the liquid extractions based on liquid-liquid precision experiments. Initial stock was 66±5% Pu(IV).*

The uptake of ^{238}Pu appeared to increase with increasing pH which was expected. The highest total Pu uptake occurred at pH 4.5 and then decreased at pH values greater than pH 4.5. The decrease at higher pH may be due to hydrolysis of Pu(IV) or oxidation of Pu(IV) to Pu(V). The uptake appeared to rise significantly among pH values greater than pH 3. Previous studies show a similar rise where Th(IV) had a sudden uptake (close to 100%) around pH 2 with 0.2 M DBM in benzene (Kobashi et al., 1993; Saito & Choppin, 1983). It would be expected that there should be a higher uptake at lower pH given that the Pu(IV) species readily complexes with DBM but this was shown not to be the case here. The uptake is thought to be primarily attributed to Pu(IV) and possibly Pu(VI) species. Unfortunately, oxidation analysis was not performed for each pH point, but the results agree well that approximate 47±5 to 66±5% of Pu species are Pu(IV) from initial OA test. Additionally, it is worth noting that this experiment was performed without triplicates and error could be significant. The recovery was approximately 100% across pH values suggesting adequate experimental technique and negligible Pu loss. The recovery decreased to 90% around pH 5, indicating some loss of Pu likely through wall sorption and precipitation at higher pH values.

pH influence on Pu extraction is complicated to study due to the separate behaviors of Pu(IV) and Pu(V). DBM is known to have little to no uptake with An(V) and high affinity for An(IV) and An(VI) actinides(Saito & Choppin, 1983). It was recommended that low pH is better when working with Pu(IV) as you will have less hydrolysis and wall sorption. A geochemical profile (**Figure 28**) shows speciation of Pu(IV) species in a system closed and open to the atmosphere (Powell & Kersting, 2008)

and can provide assistance to Pu(IV) uptake interpretations. The hydrolysis of Pu(IV) begins well before pH 2 and is a neutral species near pH 5. The exact mechanism of DBM incorporation with Pu is unknown, but the large formal positive charge on the Pu species may accelerate the complexation reaction with the DBM anion. This was shown to be the case when higher pH would result in poor kinetics for a U(VI) sample (Saito & Choppin, 1983). This suggests a competition between Pu(IV) hydrolysis and DBM incorporation of Pu(IV) likely dominates uptake and is a controlling factor.

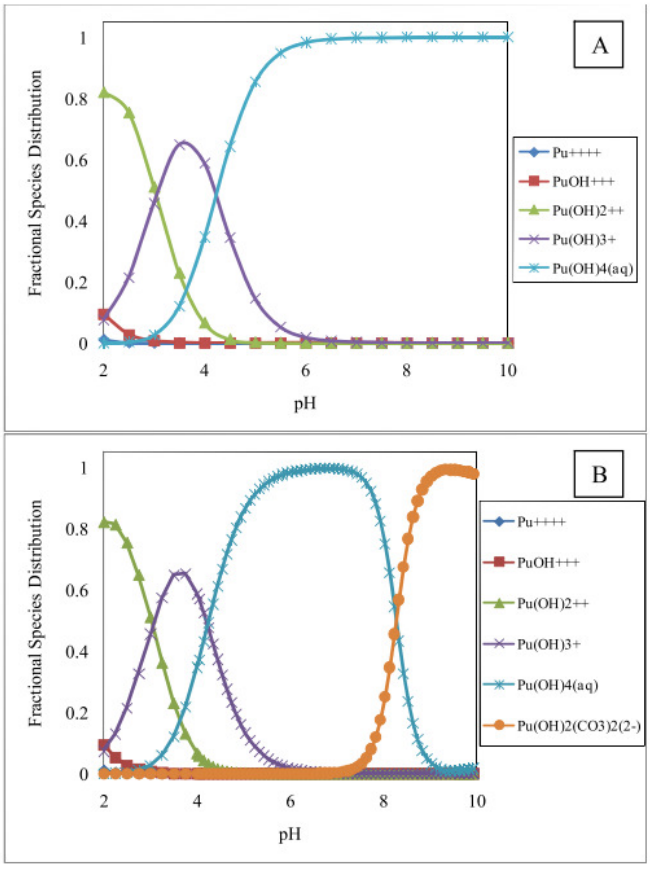

***Figure 28**: Speciation diagram showing (A) closed atmosphere and (B) open atmosphere on Pu(IV) speciation. (Powell & Kersting, 2008).*

Further experiments were performed to find optimal Pu uptake and variance among samples. From the preliminary pH experiments, it appeared that pH 4 to 4.75 had

the highest uptake. Samples were performed in triplicate to examine the experimental error when conducting a liquid-liquid extraction procedure (**Figure 29 and Figure 30**). Here, 0.6 mL of each phase was shaken for 15 minutes with 0.2 M DBM in 1-octanol. The aqueous phase was composed of ^{238}Pu (3 Bq/mL) with 0.01M acetate with a redox distribution of 47±5% Pu (IV) and 53±5% Pu(V). The highest uptake occurred at pH 4.25 with approximately 28% total Pu or 60% Pu(IV) uptake. The experimental error from each of the four samples had an average standard deviation of ±7%. A one-way ANOVA was performed with a p-value of 0.23 indicating that the four pH points had statistically the same uptake.

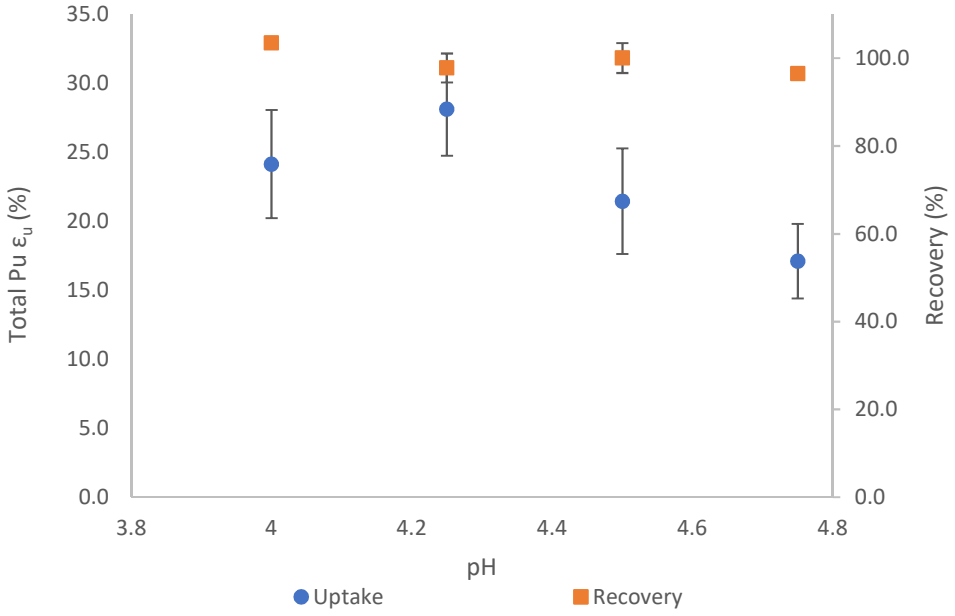

Figure 29: *Triplicates samples with total Pu uptake efficiency and recovery. Analysis performed by liquid-liquid extraction using a 0.2 M DBM in 1-octanol. Samples were shaken for 15 minutes with a 3 Bq/mL ^{238}Pu solution. Error bars are due to standard deviation. ^{238}Pu(IV) stock is 47±5%.*

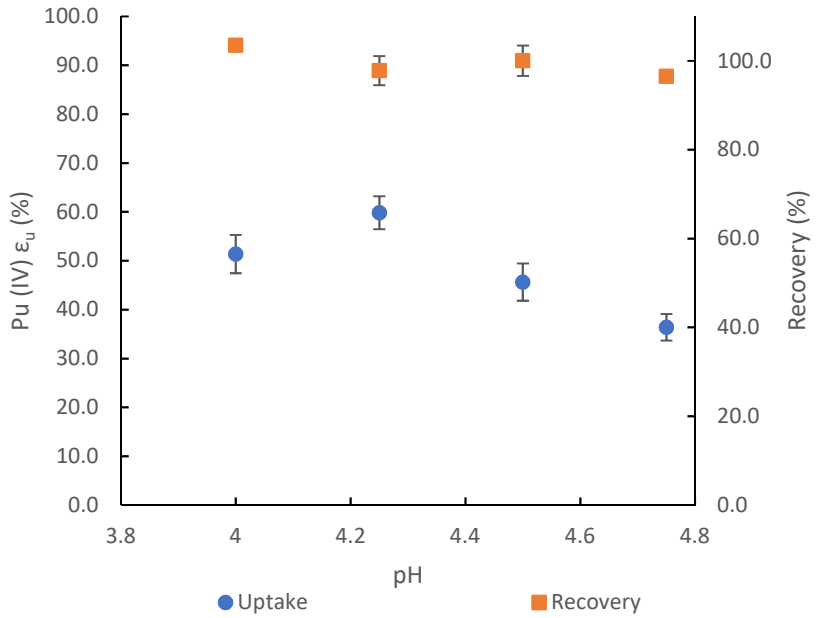

***Figure 30**: Triplicates samples with Pu(IV) uptake efficiency and recovery. Analysis performed by liquid-liquid extraction using a 0.2 M DBM in 1-octanol. Samples were shaken for 15 minutes with a 3 Bq/mL ^{238}Pu solution. Error bars are due to standard deviation.*

Liquid-liquid analysis with 0.2 M DBM in 1-octanol was also performed to investigate the degree of Pu(V) uptake. This is significant as Pu(V) is the dominant free Pu ion in most waters and there has been evidence of surface mediated reduction of Pu(V) to Pu(IV) when binding with minerals and organic matter (Conroy et al., 2017; Hixon & Powell, 2018). An experiment was designed to examine if it was possible that the DBM ligand complex could reduce the Pu(V) species to Pu(IV). A solution of

94±5% ^{242}Pu(V) at 6 Bq/mL and pH 6.4 was shaken with equal volume of 0.2 M DBM in 1-octanol for varying amount of time **Figure 31.**

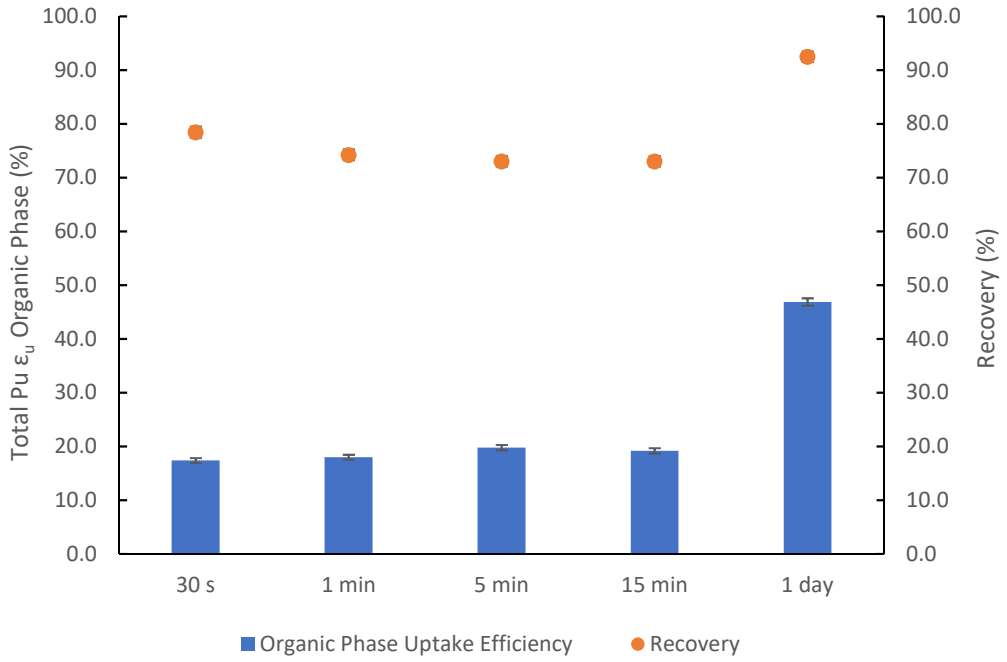

Figure 31: *Uptake efficiency and recovery of total ^{242}Pu (6 Bq/mL) from a 94% ^{242}Pu(V) solution at pH 6.4 shaken over time with 0.2 M DBM. Error is due to counting statistics.*

Approximately 20% of ^{242}Pu was immediately removed from the aqueous phase and 47% was taken up after 1 day (**Figure 31**). The increased uptake over 24 hours indicated slow uptake Pu(V) from the initial stock. The poor recovery at early mixing times indicated that approximately 25% of ^{242}Pu was not accounted for in either the organic or aqueous phase. Thus, the uptake described in **Figure 31** demonstrates Pu lost to solution and not uptake in the organic phase. The Pu lost is most likely due to wall adsorption from the remaining Pu(IV) in the solution and some Pu(V). There may be enhanced uptake due to the physical partitioning of the aqueous phase into the organic phase due to lack of prior conditioning the organic solvent with an aqueous phase. At 24 hours, the recovery climbs to approximately 93% indicating most Pu is accounted for in

both phases and that Pu sorbed to wall or precipitated are brought into the organic phase. This is likely due to the higher affinity of Pu(IV) for DBM rather than the surface wall of the vial. Although uptake was still relatively low at 24 hours, Pu(V) uptake should be factored into experiment design for DBM uptake experiments with long contact times.

5.2.3 DBM extraction chromatography Resin

The first examination of the DBM-EC resin was to investigate the extent of Pu uptake and influence of pH. Three pH values from pH 3 to 4.75 were investigated (**Figure 32**) because they previously expressed high Pu(IV) uptake with the DBM ligand from liquid-liquid extractions. Approximately 5 mg of the DBM-EC resin was placed with 3 mL of a 0.01M acetate solution of ^{238}Pu (3 Bq/mL) at 47±5% Pu(IV). Additionally, standard samples with no DBM-EC resin ("No Resin") were investigated to examine loss of ^{238}Pu from bulk solution through pH hydrolysis and wall effects. The comparison of the No Resin samples with the DBM-EC resin would provide information detailing the extent of ^{238}Pu removal purely to the presence of the DBM-EC resin. The samples were shaken for one day, centrifuged and the supernatant was counted by LSC.

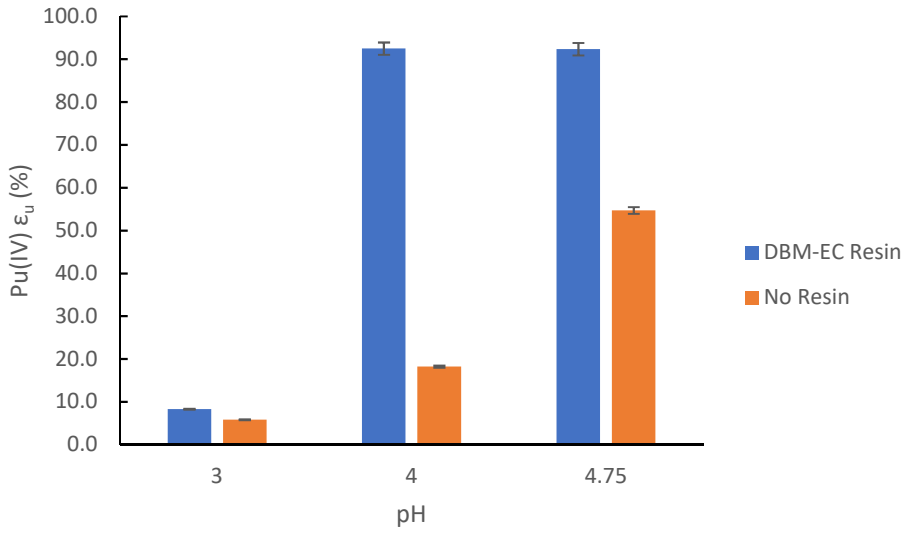

***Figure 32**: Initial DBM-EC resin ^{238}Pu uptake efficiency experiment at three different pH values at 3 Bq/mL. Error bars are due to counting error. Pu(IV) distribution is 47±5%.*

An increase in Pu(IV) uptake (or removal of Pu(IV) from bulk solution) from pH 3 to pH 4.75 was observed in both the DBM-EC resin and the "No Resin" samples. There was a sudden increase in Pu(IV) uptake in the DBM-EC resin samples between pH 3 and 4. This trend was similar to that observed from the previous liquid-liquid extraction experiments. The pH 4 and pH 4.75 solutions had approximately 92% uptake of Pu(IV), while the pH 3 solution had limited uptake, indicating that DBM uptake began between pH 3 and 4. The increase in Pu uptake with pH due to DBM ligand coincided with significant wall sorption and precipitation. The loss of Pu(IV) from solution increased from pH 4 (18%) to pH 4.75 (55%), indicating Pu(IV) competition with DBM at higher pH values. It's possible that the Pu-DBM complex is stronger around pH 4, but is overpowered by wall and hydrolysis effects as the pH increases to pH 4.75. According to the speciation plot in **Figure 28**, Pu(IV) will transition from a dominant $Pu(OH)_3^+$ to a $Pu(OH)_4$ species around pH 4. This transition into a fully hydrolyzed and neutral Pu

species likely attributes to the loss of Pu from bulk solution as pH increased in the experiment. The interpretation of the "No Resin" results only offers beginning insight into Pu loss and effects that likely hinder DBM complexation near these pH values; however, these effects are likely exaggerated because no resin was used in the wall sorption vials and addition of ligand would likely compete with wall sorption. The future addition of a blank resin with no DBM would substantially provide understanding in future experiments.

The DBM-EC resin was further subjected to an initial kinetics study to examine the rate of Pu(IV) uptake. A blank extraction chromatography with 1-octanol as a solvent and no DBM (O-EC) was used to compare against the DBM-EC resin (**Figure 33**). The solution contained 3 Bq/mL of 47±5% ^{238}Pu(IV) at pH 4.25 with 0.01M acetate. Approximately 10 mg of resin was placed with 3 mL of the ^{238}Pu solution. The samples were shaken from 15 minutes to 2 days. The samples were centrifuged and the supernatant was counted by LSC. After decanting the remaining resin, a 0.1 M HNO_3 solution was added to the vials and was shaken for 1 day. The rinse solution was then counted by LSC to observe wall sorption.

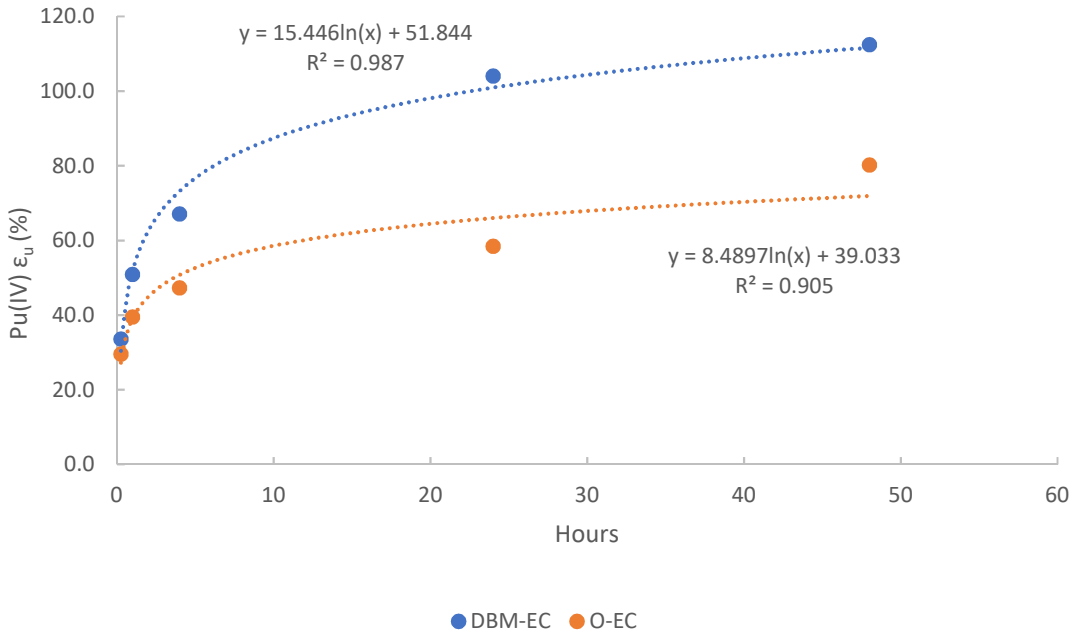

***Figure 33**: ^{238}Pu uptake efficiency over 2 days for DBM-EC and O-EC resins at pH 4.25 with 3 Bq/mL of ^{238}Pu and 0.01M acetate. Single data points only. The solution had a Pu(IV) distribution of 47±5%.*

The kinetic results show an increase in uptake ^{238}Pu for both the DBM-EC and O-EC resin over the two days with the DBM-EC resin having greater uptake at all time points. The uptake was rapid for the first couple hours while the uptake rate decreased over time. At 48 hours, the DBM-EC resin had approximately 53% percent uptake of total ^{238}Pu or approximately 100% Pu(IV) uptake, while the O-EC resin had approximately 38% of total Pu uptake and 81% Pu(IV) uptake. It was assumed that all Pu(IV) was extracted and some Pu(V) had been taken extracted after being reduced to Pu(IV) over time. The acid leach indicated approximately approximate 3% loss to the wall indicating that the majority of Pu(IV) is adsorbing to the polystyrene resin or the DBM ligand in the DBM-EC resin. The sorption of Pu to the O-EC resin was substantial and was assumed due to the natural affinity of Pu(IV) to sorb to the polystyrene surfaces at non-acidic pH.

The influence of Pu redox state with adsorption to the DBM-EC and O-EC resins was further investigated. The influence of DBM on Pu oxidation states was examined by performing oxidation analysis for an uptake experiment at 1 hour, and 24 hours (**Figure 34**). The experiment utilized a 10 Bq/mL solution of ^{242}Pu that had an approximate 50 ± 5% of both Pu(IV) and Pu(V) with trace levels of Pu(VI). The 50/50 pairing was fortunate as it allowed easy tracking of specific oxidation state uptake over time. The solution also consisted of 0.01M acetate and was at pH 4.15 with 13 mg of resins being shaken for 1 and 24 hours (**Figure 34**).

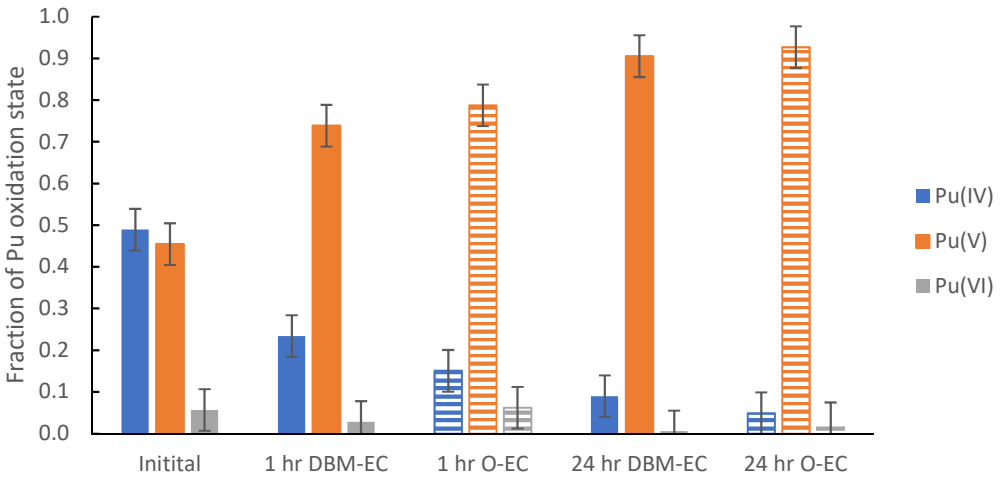

Figure 34: *Oxidation state distribution of a ^{242}Pu solution in a batch reactor with DBM-EC (solid) and O-EC resins (stripes) at 1 hour and 24 hours.*

The DBM-EC and O-EC resins demonstrated similar uptake schemes where Pu(IV+VI) was removed from solution due to sorption to the resins and leaving Pu(V) in solution. The large decrease fraction of Pu(IV) over 1 hour coincided with an increase of Pu(V) indicating that the Pu(IV) uptake was relatively rapid while Pu(V) uptake was slow or nonexistent. At 24 hours there was a decrease of Pu(IV) for both resins, however it was much slower than over 1-hour period.

The concentration of each oxidation state of the ^{242}Pu solution was quantified as well (**Figure 35**). The Pu(V) concentration remained constant while the concentrations of Pu (IV+VI) decreased throughout the 1 day of mixing for both resins. The changes in concentration agreed well with the examination of the redox fractions. The total uptake for all Pu(IV+V+VI) was slightly higher for the O-EC resin at approximately 39% to the DBM-EC resin at 35%, but this may be within error as they are single data points. These results examining total Pu uptake were unexpected, as previous kinetic data on the DBM-EC resin had almost double uptake for the DBM-EC resin compared to the O-EC resin (**Figure 33**). It is possible that DBM may have washed out from the resin bead and into solution over time. No study was performed to confirm this, but should be included with future work of extraction chromatography resin batches. An acid leach was performed on the walls of the 24-hour container indicating approximately 8% wall sorption for both resins. Additionally, it would be expected that the DBM-EC resin would have less wall sorption than the O-EC resin as the DBM supposedly forms a stronger complex compared to surface sorption.

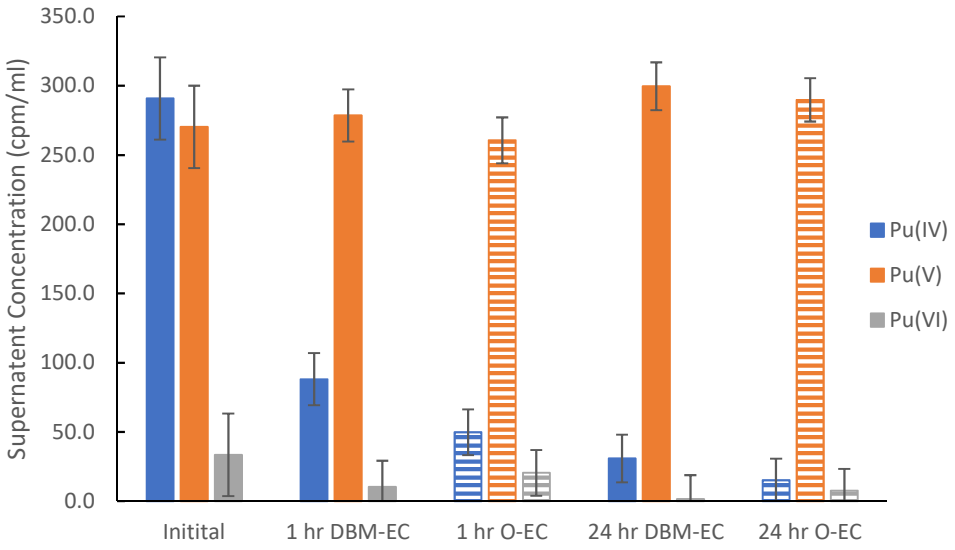

***Figure 35**: Concentrations of 10 Bq/mL of ^{242}Pu in a batch reactor with DBM-EC (solid) and O-EC resins (stripes) at 1 hour and 24 hours.*

A supplemental experiment (**Figure 36**) was performed to examine aging with the DBM-EC resins, specifically with a new or fresh DBM and a 4-month old DBM-EC resin. This is because the DBM-EC resin that was used in the redox experiments (**Figure 34 and Figure 35**) was from a new and different batch of resins that were made four-months after the original DBM-EC resin used in **Figure 33**. In these previous experiments, the "old" DBM-EC resin expressed enhanced Pu uptake when compared to the O-EC resin whereas the "new" DBM-EC resin had an identical uptake profile as the O-EC resin. A solution of 7 Bq/mL of ^{242}Pu was titrated to pH 4.25 with 0.01M acetate and 10 mg of resin. The solution was mixed for 24 hours and the supernatant was counted. The old and new DBM-EC resins had relatively the same uptake, while the O-EC resins had a slight decrease. This indicated that the old and new DBM resins had similar uptake profiles and were likely functioning the same (**Figure 36**). The lower

uptake of the O-EC resin could be due the presence of DBM, however no triplicates were taken and could be within the same uptake range as the DBM-EC resins.

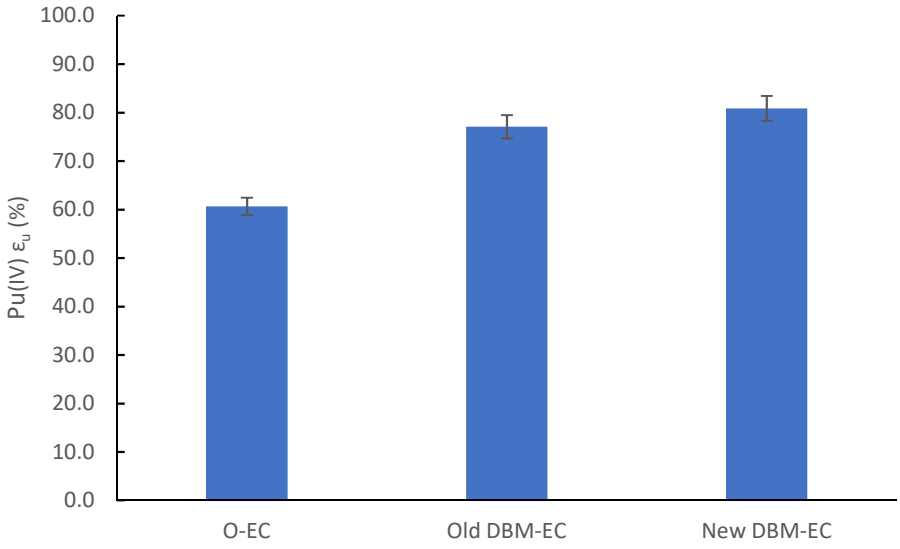

***Figure 36**:Pu(IV) uptake efficiency for a 7 Bq/mL ^{242}Pu solution with 24-hour shake at pH 4.25 with 0.01 M acetate. The old and new DBM were made approximately 4 months apart. Error is due to counting error. The Pu(IV) distribution is 49±5%.*

To differentiate the affinity of Pu(IV) for DBM and polystyrene surface-sorption, an experiment was tested on a low pH sample (**Figure 37**). The experimental solution was a 7 Bq/mL ^{242}Pu solution at pH 2 with 56 ± 5% Pu(IV) with 12 mg resin. The samples were shaken for an hour, counted by LSC and were later acid-leached to examine wall sorption. The Pu(IV) uptake for the DBM-EC resin was substantially higher than the O-EC resin at 62.7±1.5% and 25.2±0.6%, respectively. The difference in uptake of the DBM-EC and O-EC resins was likely attributed to the DBM ligand while the O-EC resin uptake portion represents non-ligand surface sorption of Pu(IV) to the resin. Wall adsorption of Pu(IV) was also low at approximately 2% for both samples. The results indicated that Pu extraction, solely due to the DBM ligand, occur around pH 2

where Pu(IV) exits as a less hydrolyzed species. Because of the low pH, it is expected that kinetics will be slower and will require longer contact time with DBM. This was demonstrated with other actinides and DBM by Saito & Choppin, 1983.

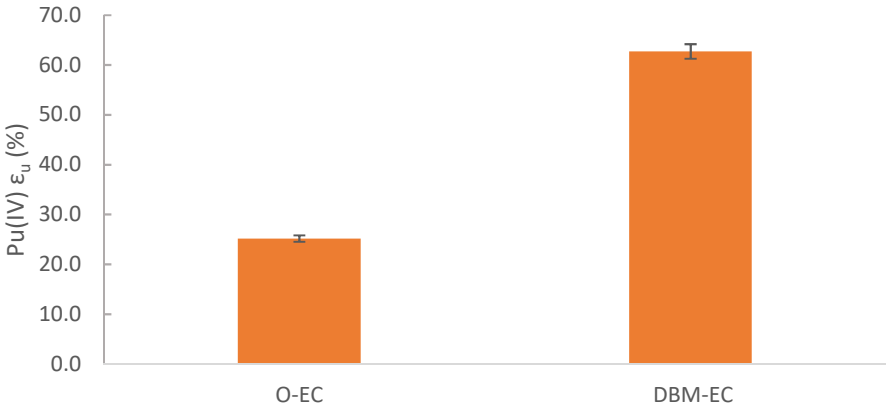

***Figure 37**: Uptake efficiency for a 7 Bq/mL ^{242}Pu(IV) solution at pH 2 using EC resins shaken for 1 hour. Error bars represent counting error. The solution has a Pu(IV) distribution of 56±5%.*

A column experiment was performed to examine uptake behavior with column geometry for the DBM-EC resin. 30 mg of DBM-EC resin and 90 mg of O-EC resin were packed in a column of PFA tubing with 1/16" inner diameter. A peristaltic pump was used to pump a ^{238}Pu solution at approximately 0.2-0.4 mL/min. The 7 Bq/mL ^{238}Pu solution was pH 4.22 and the initial oxidation analysis indicated a Pu(V) dominant distribution (81±5% Pu(V), 16±5% Pu(IV) and 2±5% Pu(VI)). Uptake for Pu (IV+V+VI) for the DBM-EC resin was relatively constant at approximately 25% while the O-EC resin had a decrease in Pu uptake over increasing loading. The low Pu uptake is likely due to Pu(IV) and Pu(VI) uptake with the resins with little Pu(V) being retained. The constant rate of Pu uptake in the DBM-EC resin vs the decline in uptake in O-EC resin likely indicated that Pu was retained by the DBM ligand in the DBM-EC resin, while the Pu uptake in the O-EC resin decreased due to weak electrostatic binding to polystyrene

surface and exceeding resin capacity or equilibrium changes after loading 4 mL. This could be significant, because previous batch experiments indicate significant Pu(IV) sorption to the O-EC resin at pH 3-5 solutions. The column flow geometry could provide a future method to distinguish uptake of Pu due to the DBM ligand in the DBM-EC and O-EC resins.

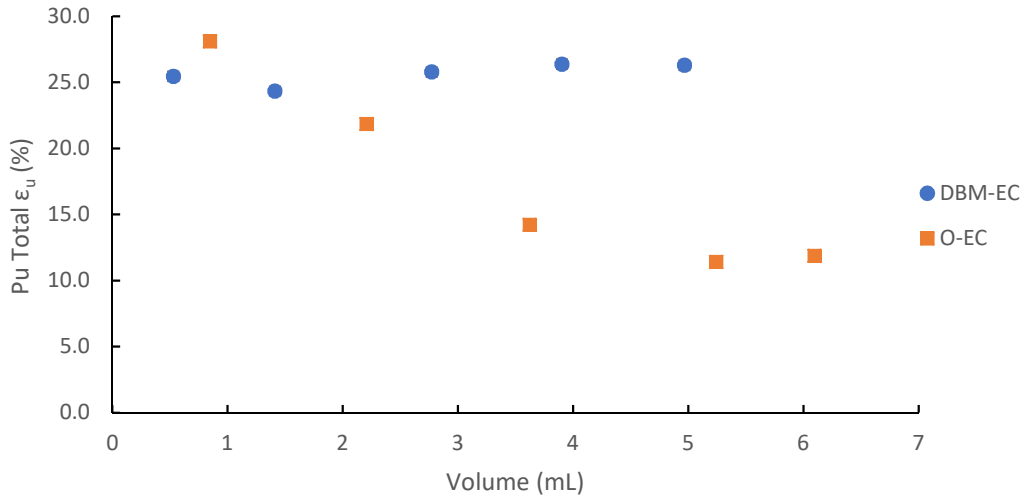

***Figure 38**: Total ^{238}Pu uptake efficiency as a function of column flow for a 7 Bq/mL ^{238}Pu solution using a peristaltic pump. Error bars are due to counting error. Solution is 16±5% Pu(IV) and 81±5% Pu(V).*

5.2.4 Scintillation and detection of DBM-EC resin

The next step in the progression of developing a scintillating resin required characterization of a scintillating DBM extraction chromatography resin. The scintillating resin was made in the same way as the extraction chromatography (EC) resin, but with a resin base that contained scintillating material. Specifically, this porous resin was 106-212 µm porous bead composed of PVT plastic and αNPO as the fluor.

The fluor was incorporated into the bead via suspension polymerization (Gokmen & Du Prez, 2012). The ligand was impregnated in the scintillating resin core as 0.2M DBM in 1-octanol (S-DBM-EC). A replica of the S-DBM-EC resin was made without the DBM ligand but still retained the 1-octanol solvent incorporated within (S-O-EC).

The radioluminosity and detection efficiency (ε_d) were evaluated following batch uptake experiments. This required mixing 10 mg of resin with a 3 mL of 48 Bq/mL ^{238}Pu (22±5% Pu(IV), 65±5% Pu(V), and 12±5% Pu(VI)) in a pH 3.9 solution with 0.01M acetate. Samples were shaken for 1-hr and 24-hr and then centrifuged. The supernatant was counted by LSC. The 24-hr resin beads were loaded into a 5-cm PFA tube and allowed to dry to constant mass. Once dry, the loaded resin columns were dark adapted overnight and then counted on the LSC for 30 minutes. Along with the S-DBM-EC and S-O-EC resins, scintillating beads with no solvent (No-EC) were counted as well to examine influence of the 1-octanol.

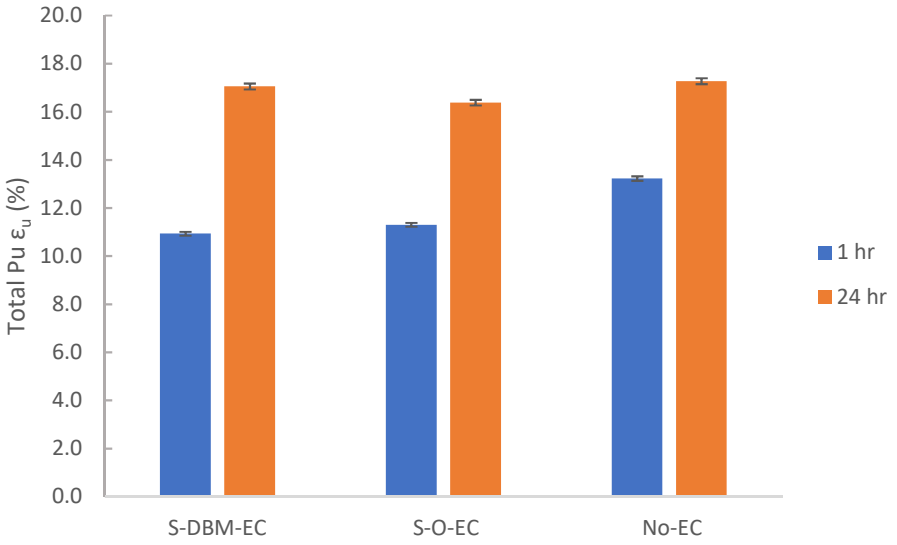

***Figure 39**: Total ^{238}Pu uptake efficiency uptake after 1-hr (blue) and 24-hr (orange) of shaking for the various extraction chromatography resins. Solution is 22±5% Pu(IV) and 12±5% Pu(VI) at pH 3.9 at 48 Bq/mL.*

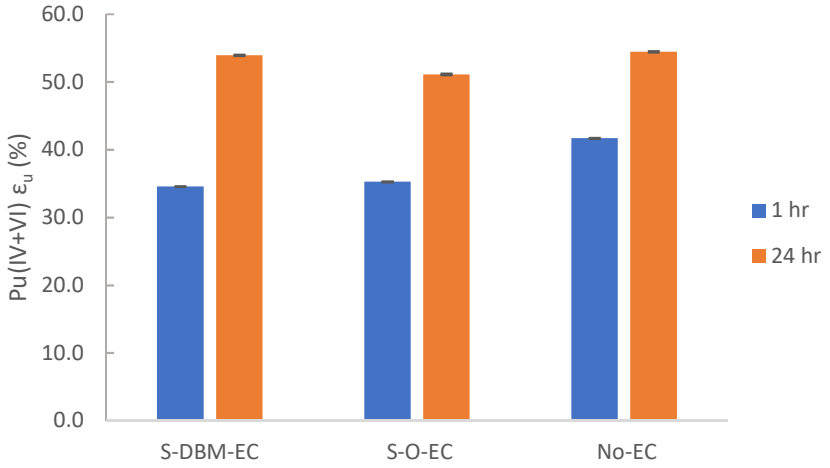

***Figure 40:** Uptake efficiency of ^{238}Pu(IV+VI) after 1-hr (blue) and 24-hr (orange) of shaking. Solution is 22±5% Pu(IV) and 12±5% Pu(VI) at pH 3.9. Solution is 48 Bq/mL of total ^{238}Pu.*

The uptake of ^{238}Pu with the extraction chromatography resins is demonstrated in **Figure 39 and Figure 40.** The S-O-EC and No-EC resins had similar ^{238}Pu uptake as the S-DBM-EC resin for both 1 hour and 24 hours. This was a similar trend that had been observed in the non-scintillating resins (DBM-EC and O-EC) that had Pu(IV) adsorbing to the resin bead to the same extent even without the DBM ligand. There was an increase

in total Pu and Pu(IV+VI) uptake from 1 hour to 24 hours and the majority of Pu(IV+VI) was removed within one hour indicating relatively fast kinetics. Although the No-EC resin appeared to have the highest uptake, the increase in uptake without 1-octanol is considered minimal at best and could be within experimental error. The explanation why No-EC and the O-EC resins have Pu extraction at a similar extent as the DBM-EC could be from Pu(IV+VI) adsorbing to the resin due to presence of functional groups on the polystyrene resin as a more hydrolyzed Pu species.

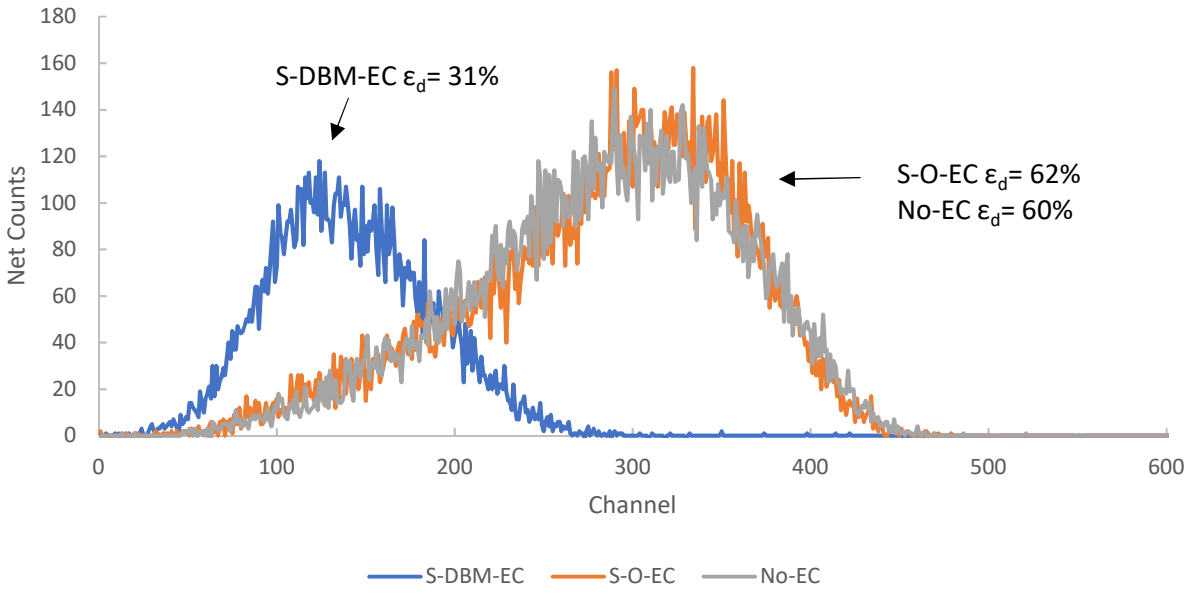

***Figure 41**: Spectrum of the loaded scintillating resins with ^{238}Pu.*

The ^{238}Pu-loaded resins were counted by LSC to obtain spectrum and detection efficiencies (**Figure 41**). All three resins expressed radioluminosity as peaks were observed in all resins. This is expected due to the presence of scintillator and the uptake of Pu(IV+VI) in the batch experiment. The S-O-EC resin and No-EC resin had near identical spectrum while the S-DBM-EC resin appeared to be significantly quenched. It was inferred that this was due to the DBM ligand because 1-octanol in the S-O-EC resin

did not result in quench. The quenching is a serious concern as it can impact detection efficiency. The S-DBM-EC resin had a detection efficiency (ε_d) approximately 31% which was half of the S-O-EC resin and No-EC resin at 62% and 60%, respectively.

The DBM quench could be due to chemical or color quench. Chemical quench with DBM was investigated as it would prevent the absorbance of the UV light in the vNPO fluorophore (**Figure 42**). The absorbance of the vNPO fluorophore was previously investigated and determined to have 336 nm peak in a methyl acetate solution (Seliman et al., 2015). It is likely that DBM has absorbance near this range and could be problematic for use in scintillating resins.

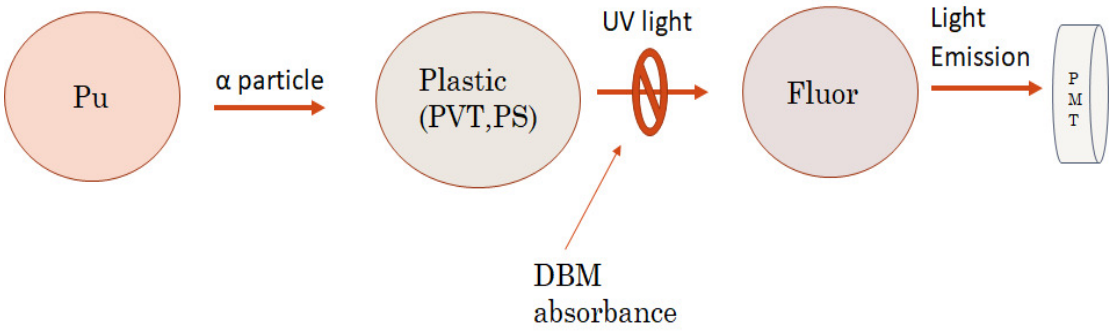

***Figure 42**: Schematic of DBM chemical quench in the scintillating resin.*

The absorbance of the DBM ligand in 1-octanol was investigated using a UV spectrophotometer. Approximately 3mL of solution was placed in plastic cuvettes and an absorption spectrum was obtained for wavelengths of 200-800 nm (**Figure 43**). In order to observe the max peak, the concentration of DBM had to be diluted from 0.2 M to 10^{-5} M. The absorption peak occurred at 345 nm which was well within the absorption region for the vNPO fluor. This indicated that DBM did indeed result in chemical quench and would not be a suitable ligand for extractive scintillating resins using the vNPO fluor.

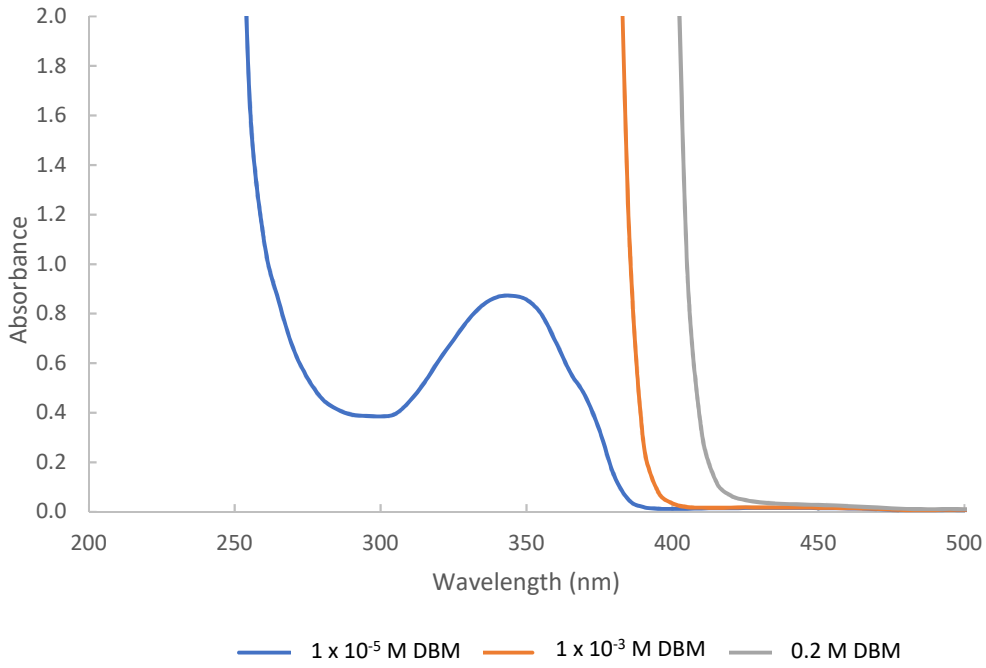

***Figure 43**: Absorption spectra of DBM in 1-octanol at various concentrations.*

CHAPTER SIX

CONCLUSION

Extractive scintillating resins have potential to be a valuable tool for environmental monitoring of Pu. The behavior of Pu is complex and therefore detection techniques must be well established before implementation of real-world applications. This research aimed to address the challenges of Pu quantification in aqueous systems by examining matrix influences on Pu extraction, evaluating radioluminosity through additions of scintillator, and by testing with different experimental set-ups. This was accomplished by developing an Analig® Pu02 extraction resin with scintillator and by creating a scintillating DBM extraction chromatography resin.

The Analig® Pu02 resin was successfully modified and expressed good Pu uptake and adequate scintillation. Several modification parameters such as particle size and modification time were investigated. It was determined that a 6-hour silanization and 12-hour polymerization time with small particle size would result as the highest performing resins. In addition to off-line detection measurements, a modified Analig® Pu02 resin was subjected to real-time measurements where on-line loading of Pu was successfully detected. The modified Analig® Pu02 resin further demonstrated that other groundwater ions did not affect performance other than at high concentrations (10^{-3} M) of Fe(III). Based on the results, the modification of the modified Analig® Pu02 resin can detect moderate to low concentrations of Pu by manipulating key experimental variables that indicate a potential to be applied to real-world groundwater samples.

Although the modification was successful for Pu detection, there were many challenges with working on the modification of the Analig® Pu02 resin. The primary difficulty consisted of working with a proprietary product with little known about the extractant on the surface. This significantly limited the potential of understanding the extraction of Pu on a chemical level. Understanding the chemistry of Pu and ligand interactions in certain environments is imperative to maximize extraction and increase selectivity. Overall, the modification of Analig® Pu02 proved to be successful and indicated promise for future experiments involving modification of other extractive resins with silica supports.

There were several attempts of Pu detection with a scintillating DBM extraction chromatography resin. Many experiments had to be performed in order to obtain a general behavior of Pu and DBM interactions. The DBM ligand in both liquid-liquid extractions and extraction chromatography resin with 1-octanol was capable of extracting Pu, but was highly dependent on pH and redox chemistry. Pu(IV) was the primary species of Pu to be extracted. Pu(V) uptake with the DBM extraction chromatography resin was slow and required long contact time for even modest uptake as the Pu(V) was reduced to Pu(IV) in the presence of the resin. The highest extraction for the DBM extraction chromatography resin occurred near pH 4; however, other control resins with no ligands were shown to have similar uptake profiles at this pH. Plutonium uptake solely due to the presence of DBM was shown to be favorable at pH 2, albeit slow and with lower extraction as compared to pH values near 4. This was likely due to the

protonation of the DBM anion at lower pH. At higher pH values, significant wall sorption and hydrolysis effects would dominate extraction of Pu(IV).

The incorporation of the DBM ligand to a polystyrene resin resulted in no obvious enhancement of Pu uptake. This was likely due to leaching of DBM ligand into solution or Pu(IV) sorption to the resin bead surface and not by DBM complexation. The incorporation of DBM with a scintillating resin beads demonstrated that the DBM ligand significantly quenched light output by absorbing UV light at 345 nm. This was a significant problem as many the fluor used for extractive scintillating resins have an absorption wavelength near this range. Overall, the DBM ligand was a poor extractant for aqueous Pu at low to circumneutral pH and would not be an optimal candidate for a Pu extractive scintillating resin. Significant preconditioning of pH and redox speciation in a sample would need to occur for even a modest extraction of Pu with DBM which would defeat the purpose or ease of using an extractive scintillating resin.

Future Work:

There was significant variability with the performance of the modified Analig® Pu02 resin. Several factors were addressed, but a more rigorous examination of variables should be performed. Additionally, other supports should be investigated. The ability to optimally and consistently attach scintillator to extraction resin for any target analyte would be an invaluable tool.

Additional work with the modified Analig® Pu02 resin would require further characterization with variable such as pH, organic matter, and selection of eluents. This however, may be difficult to achieve until the propriety ligand is known.

Plutonium uptake with DBM ligand was difficult to achieve due to hydrolysis and surface sorption effects. This indicates, that DBM may not be a good candidate for reliable Pu extraction. However, other actinides with stable chemistry in slightly acidic to circumneutral pH should be investigated. Having an extractant that works well at circumneutral would require less preconditioning and be an incredible asset as an extractive scintillating resin for environmental monitoring.

Many organic ligands are capable of extracting Pu(IV), however Pu(V) extraction remains non-existent or kinetically limited. Further research needs to investigate possible ligands of extracting Pu(V) more efficiently and timely as it is a dominant form of Pu in environmental samples. If this cannot be achieved by a ligand, more research needs to be

applied to preconditioning environmental samples to transform a Pu(V) species into a more Pu-extractable form.

It would be advantageous to have a covalently-bound ligand capable of extracting Pu. This is an incredibly complex task, but worthy of further investigation. A ligand that could work at low pH may be best as it would be able to extract Pu(IV) more efficiently and make experimentation more efficient.

APPENDICES

Appendix A

Analig® Pu02 uptake of Pu(V)

Pu(V) uptake was investigated using the Analig® Pu02 even though the resin was originally designed for Pu(IV). Having an ability to uptake Pu(V) and be relatively quick would be a tremendous benefit for environmental monitoring of Pu as Pu(V) constitutes a large portion of mobile and difficult to capture fraction of Pu. Here, 10 mg of Analig® Pu02 was mixed with a pH 6.4 ^{242}Pu solution with approximately 85±5% Pu(V). The resin and Pu solution were mixed for varying time up to 24 hours (**Figure A-1**, 24 hours not shown). The samples were centrifuged and the supernatant was counted by LSC.

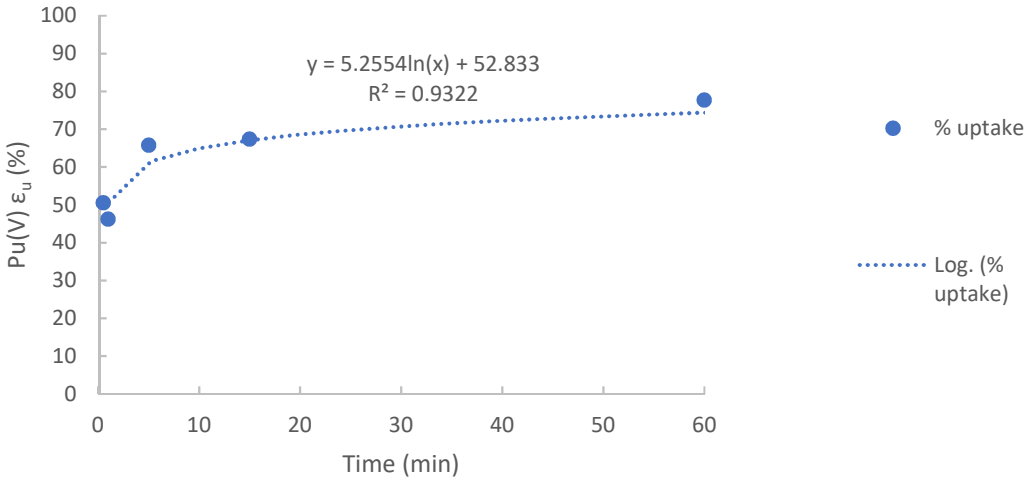

Figure A-1: *Pu(V) uptake with Analig® Pu02 (24-hr point is not shown).*

There appeared to be an immediate uptake of Pu which is likely a loss of Pu due to the Pu(IV) fraction adsorbing to wall or precipitating out. There is a continual rise in uptake up to 24 hours where uptake is approximately 90% (not shown). The results indicate that Pu(V) uptake is kinetically limited, because approximately 80% of Pu is

removed from solution within an hour. This is could be due to Pu(V) complexing with the high affinity ligands of the Analig® Pu02, however it is also likely that Pu(IV) was sorption was contributing due to the initial Pu(IV) that was sorbed to walls and the surface mediation reduction of Pu(V) to Pu(IV). The results of the experiment indicate that Analig® Pu02 could work for circumneutral pH and collect both fraction of Pu(IV) and Pu(V) if long contact time. Also, the results indicate that most fraction of Pu should be extracted as long as several hours of mixing time are observed.

Appendix B

Analig Pu02 Modification Procedure

The Analig Pu02 resin was modified by two different methods. The first method involved CMA(1-5) while, the second method was incorporated for the evaluation of particle size and time of modification. Although different methods, they are similar with only few differences.

Method 1

1. The raw Analig Pu02 resin was crushed by mortar and pestle for 15 minutes. The resins were soft and were crushed easily due to their porous composition.
2. 250 mg of the crushed resin was placed in a glass beaker with 5 mL of toluene. 125mg of 3-methacryloxypropyltrimethoxysilane (MPS) was added. The solution was mixed in a lab-hood for approximately 12 hours with no heat addition. The mixer consisted of an overhead IKA® RW 11 stirrer with a flat-blade impeller. Toluene was added if solution was evaporating too quickly.
3. After 12 hours of mixing, the solution was filtered onto a Whatman filter paper. The solution was then washed with 20 mL of toluene and then 20 mL of ethanol. The resin was allowed to dry for approximately one day.
4. 250 mg of the silanized resin was placed into a 200 mL three-necked round bottom flask. Next the following were added: 50 mg of vNPO, 250 mg p-methylstyrene (98%, Arcos Organic), 20 mg Azobisisobutyronitrile (AIBN, 98% Sigma Aldrich), and 10 mL toluene. The methylstyrene previously had inhibitor

removed by running the solution through a column of alumina. The solution was mixed by the IKA® RW stirrer with a round spatula and began heating to 70°C in a sand bath. While mixing and heating, high-purity nitrogen gas was pumped for 15 minutes. The mixture was then closed by inserting a condensing column and running cold water through it. The solution was refluxed and mixed at 70°C for approximately 12-24 hours.

5. After polymerization, the mixture was filtered onto a Whatman filter paper. The solution was then washed with 20 mL of toluene and then 20 mL of ethanol. The resin was allowed to dry for approximately one day. The modified resin was then ready to begin uptake and radioluminosity experiments.

Method 2

1. The raw Analig Pu02 resin was crushed by mortar and pestle for 15 minutes. The resins were then sieved based on particle size using sizes <63 μm, 63-106 μm, and 106-180μm.
2. 600 mg of crushed Analig Pu02 resin was placed within a single-neck round bottom flask in addition to 5 mL of toluene and 300 mg of MPS. A magnetic stir-bar was inserted rather than an overhead impeller. The solution was then heated to 50°C in a sand-bath. While heating, the solution was bubbled with nitrogen gas for 15 minutes. The flask was then capped with a condenser column and allowed to mix and refluxed for 6-12 hours at 50°C.
3. After silanization, the solution was filtered onto a Whatman filter paper. The solution was washed with 20 mL of toluene and then 20 mL of ethanol. The resin

was allowed to dry for approximately one day and then sieved to obtain particle size distribution.

4. 300 mg of the silanized resin was mixed with 5mL toluene, 60 mg vNPO, 300 mg of methylstyrene monomer (removed inhibitor), and 20 mg of AIBN. The mixture was heated and mixed in a 200 mL round bottom single-neck flask. The mixing performed by a magnetic stir bar at 70°C. The mixture was bubbled with nitrogen gas for 15 minutes prior to refluxing with a condenser column. The polymerization occurred for 12-24 hours at 70°C.
5. After polymerization, the solution was filtered with a Whatman filter paper. The resin was washed with 50 mL of ethanol. The resin was allowed to dry for approximately one day and then sieved to obtain particle size distribution. The modified resin was then ready to begin uptake and radioluminosity experiments.

Appendix C

Uptake studies of DBM modifications

Several modifications of DBM were attempted as a goal to create a DBM monomer that can be covalently attached with a scintillating polymer. Liquid-liquid extractions were performed on the DBM intermediates to determine if modification of ligand influenced Pu uptake. The first DBM intermediates tested (**Figure C-1**) were 1-(4-Bromo-phenyl)-3-phenyl-propane-1,3-dione (BrDBM) and 2-Methyl-acrylic acid 4-(3-oxo-3-phenyl-propionyl)-phenyl ester (mDBM). The ligands were dissolved in 1-octanol as 0.2M mDBM and 0.1M BrDBM due to solubility constraints. In addition, a 0.2M DBM sample was tested that was 1 week old and unrefrigerated. The liquid-liquid extractions utilized 0.6mL each of an organic phase and a ^{238}Pu solution with approximately 50±5% Pu(IV) at pH 4.2 and 4.4. The samples were shaken for 5 minutes, although it was later determined that future contact times be at least 10 to 15 minutes.

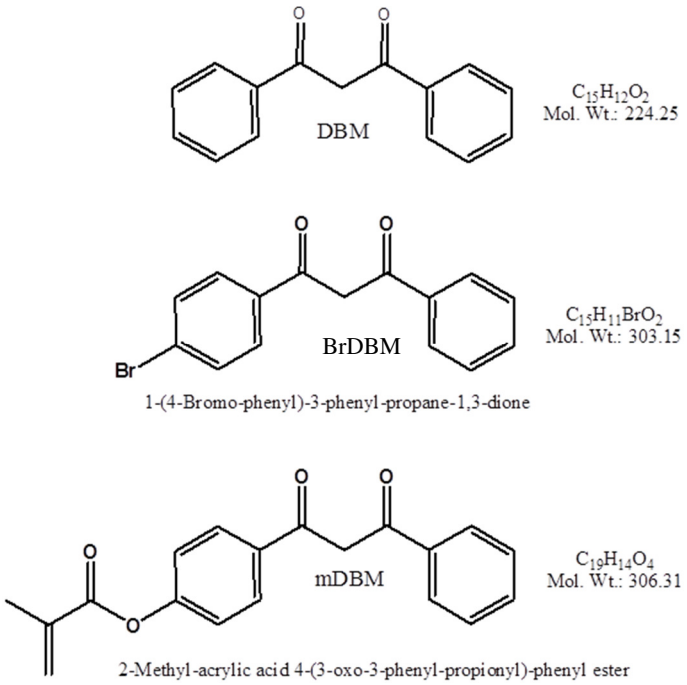

Figure C-1: *DBM intermediates used in development of a DBM monomer.*

Uptake of Pu occurred in both the mDBM and BrDBM ligands (**Figure C-2**), however, the highest uptake of Pu occurred in the 0.2 M DBM solutions at pH 4.4 with approximately 28% total Pu uptake in both samples. The one week old 0.2 M DBM sample had a lower Pu uptake at pH 4.2, but this may be due to experimental error as a 7% error is applied to the liquid-liquid extractions (7% error is from the triplicate experiment) indicating that refrigerating the sample had no influence on DBM uptake. The mDBM ligand had the lowest uptake at 7% total Pu uptake for pH 4.4 and indicated a decrease performance due to the attachment of the methacrylate arm. Recovery of Pu was near 100% showing no loss of plutonium to wall sorption or hydrolysis. Although

overall uptakes are low due to short shaking time, the results indicate that some DBM modification will likely not inhibit Pu uptake.

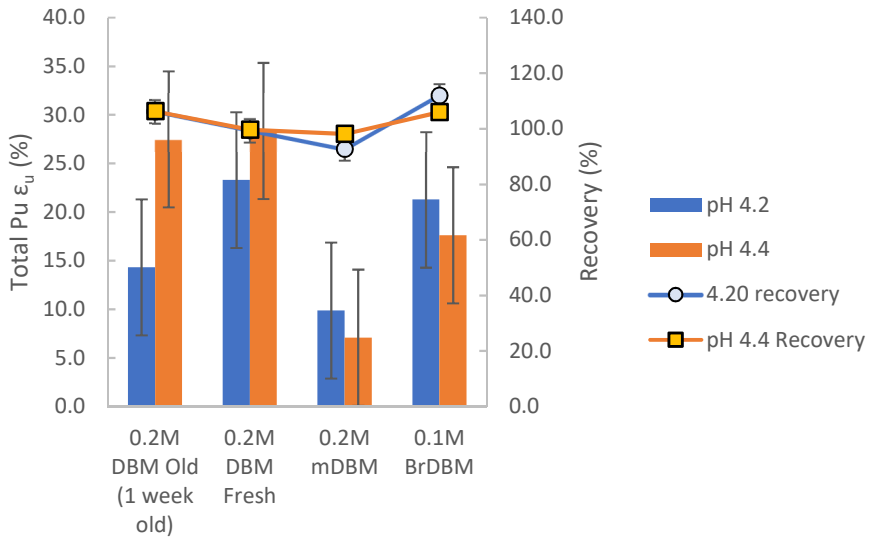

Figure C-2: *DBM intermediates tested using a 47% ^{238}Pu(IV) solution. A 7% error is applied to liquid-liquid extractions.*

Two additional DBM derivatives were tested (**Figure C-3**) to examine how structure of DBM influences Pu uptake. Methoxy-DBM was generated as an intermediate to the development of a DBM monomer. Avobenzone, a commercially available chemical that is the active ingredient in many sunscreen lotions, was also examined. The uptake of these DBM modification were tested using a liquid-liquid extraction scheme similar to previous experiments used in **Figure C-2**, with the exception of use of benzene as the solvent. Here, Methoxy-DBM was insoluble with 1-octanol, and thus benzene was used due to its non-polar properties and prevalence in

literature as a solvent for DBM extraction.

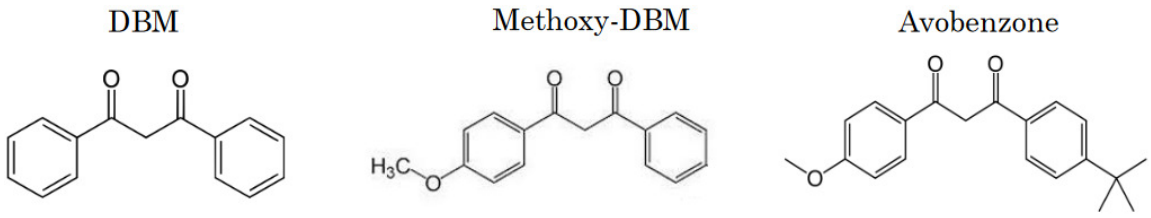

Figure C-3: *List of further DBM intermediates.*

The liquid-liquid extraction consisted of using 0.6 mL of the benzene phase and 0.6mL of an aqueous phase. The aqueous phase was a ^{238}Pu solution with approximately 47% Pu(IV) at pH 4.5. A preliminary experiment used no acetate resulting in poor uptake. Significant wall sorption effects (Not shown) and thus a subsequent experiment utilized 0.01M acetate. Shaking times were performed at 5 minutes and 30 minutes to also examine kinetics.

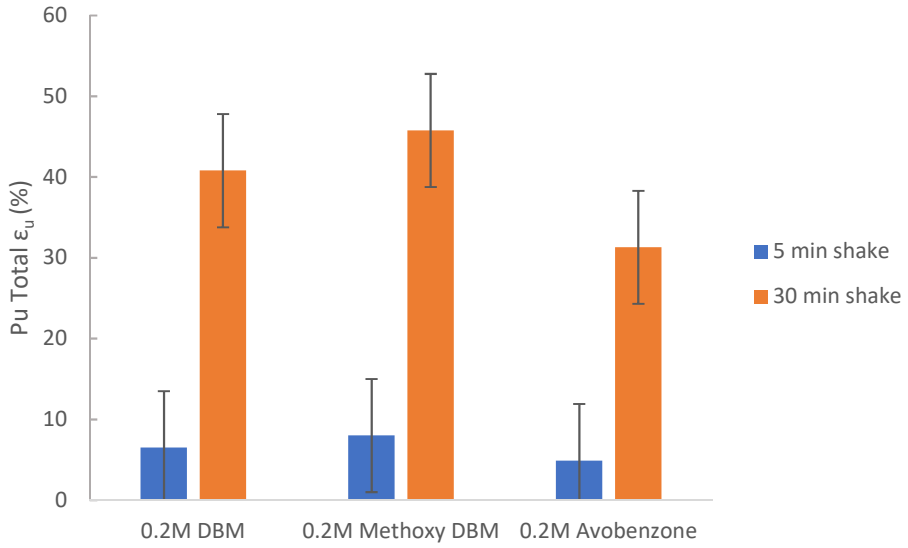

Figure C-4: *Uptake of a pH 4.5 ^{238}Pu solution with 47% Pu(IV). Error bars are 7% error applied to liquid-liquid extractions.*

Uptake for all intermediates had a substantial increase in total Pu uptake from 5 minutes to 30 minutes (**Figure C-4**). This indicates relatively slow sorption kinetics. The 0.2M methoxy DBM the highest total Pu uptake at 46% which corresponds to a complete uptake of Pu(IV). The other ligands all were within error indicating no difference in Pu uptake and showed majority uptake of Pu(IV). Although slightly lower uptake, the Avobenzone had significant uptake over the 30-minute shaking time and could provide an inexpensive alternative to study Pu uptake. The results are promising as derivatives of DBM may enhance or not decrease Pu uptake leading to promising application of a DBM monomer.

Appendix D

DBM extraction chromatography resin procedure

1. Dibenzoylmethane (DBM) was mixed with 1-octanol to make a concentration at 0.2 M DBM. Solubility was slow, and thus placing solution in hot water bath aided in dissolution of the DBM solid.
2. 0.2 M DBM in 1-octanol was added to 5-25 mL of methanol. The volume of methanol should be enough to suspend resin particles and evenly mix. The resin used was Amberchrome Tosohaas CG-3000-C 120 μm polystyrene resin beads. The mass of 0.2M DBM in 1-octanol that was required was 40% of the resin mass.
3. The resin, methanol, and 0.2 M DBM was mixed for 1 day in an IKA RV 10 Rotary Evaporator. No heat or vacuum was applied. This was to ensure that the 0.2 M DBM in 1-octanol would penetrate into the resin bead.
4. After 1 day of mixing, a vacuum and a 40°C water-batch was applied to the solution mixing in the rotary-evaporator. After several hours, the methanol would evaporate and the resin would be dry with 0.2M DBM in 1-octanol entrained within the resin bead.
5. The resin was then dried in a lab-hood for one day to ensure most of the methanol was evaporated.

Appendix E

Confocal microscopy

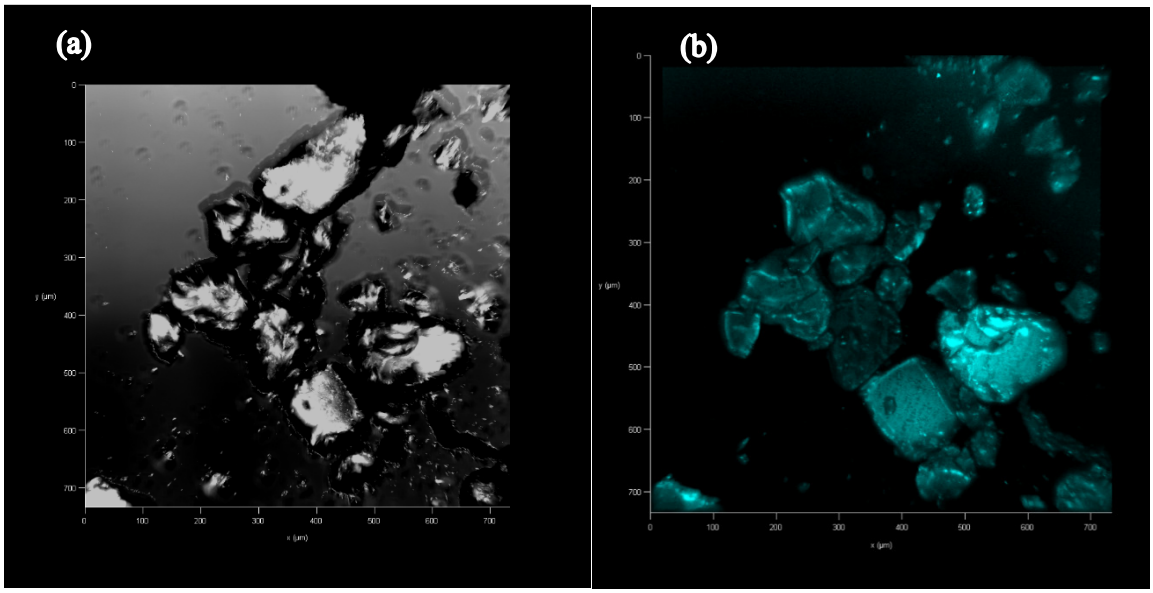

Figure E-1: *Confocal micrograph images of CMA-6S12P resin of 106-180µm. (a) Light image with no laser. (b) fluorescence (cyan color) layered with light image.*

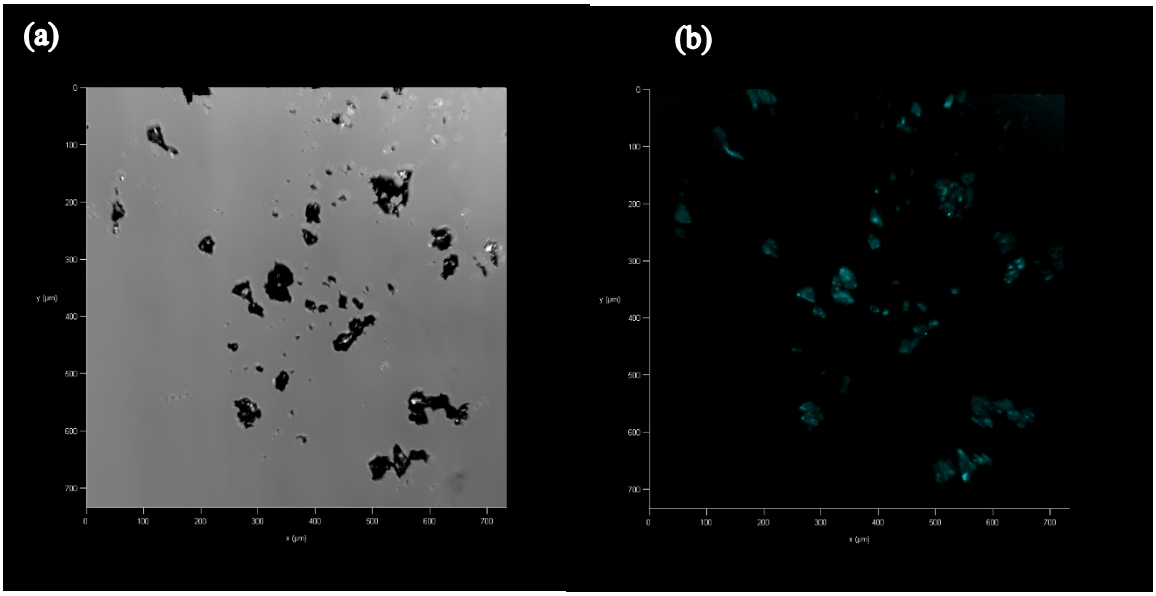

Figure E-2: *Confocal micrograph images of CMA-6S12P resin of <63µm. (a) Light image with no laser. (b) fluorescence (cyan color) of fluor due to laser.*

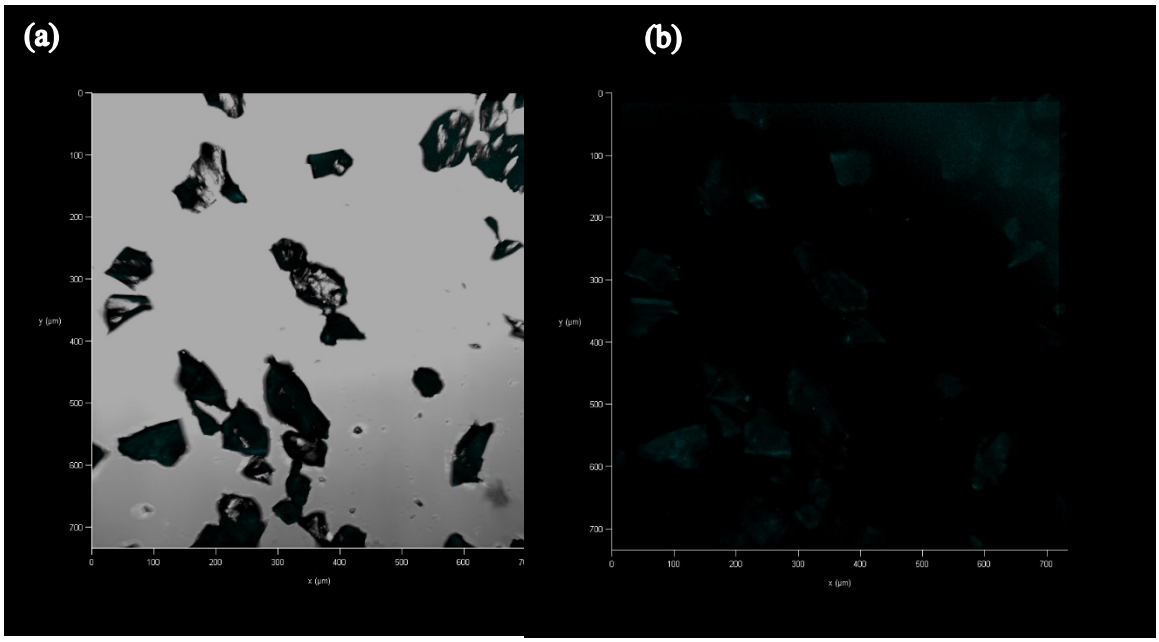

Figure E-3: *Confocal micrograph images of uncrushed-modified Analig® Pu02. (a) Light image with no laser. (b) fluorescence (cyan color) of fluor due to laser. Note the difficulty in observing the fluorescence.*

REFERENCES

Alvarez, R. (2005). Reducing the Risks of High-Level Radioactive Wastes at Hanford. *Science & Global Security*, *13*(1–2), 43–86.

Bliznyuk, V. N., Duval, C. E., Apul, O. G., Seliman, A. F., Husson, S. M., & DeVol, T. A. (2015). High porosity scintillating polymer resins for ionizing radiation sensor applications. *Polymer (United Kingdom)*, *56*, 271–279.

Cember, H., & Johnson, T. . (2009). *Introduction to Health Physics* (4th ed.). McGraw-Hill.

Choppin, G. R. (2006). Actinide speciation in aquatic systems. In *Marine Chemistry*, 99, 83–92).

Choppin, G. R., Bond, A. H., & Hromadka, P. M. (1997). Redox speciation of plutonium. *Journal of Radioanalytical and Nuclear Chemistry*, *219*(2), 203–210.

Choppin, G. R., & Morgenstern, A. (2000). Radionuclide separations in radioactive waste disposal. *Journal of Radioanalytical and Nuclear Chemistry*. Kluwer Academic Publishers.

Clark, D., Janecky, D., & Lane, L. (2006). Science-based cleanup of Rocky Flats. *Physics Today*, *59*(9), 34.

Clark, D. L., Hecker, S. S., Jarvinen, G. D., & Neu, M. P. (2008). Plutonium. In *The Chemistry of the Actinide and Transactinide Elements*, 813–1264. Dordrecht: Springer Netherlands.

Coates, J. T., Fjeld, R. A., Paulenova, A., & DeVol, T. (2001). Evaluation of a rapid technique for measuring actinide oxidation states in a ground water simulant. In *Journal of Radioanalytical and Nuclear Chemistry*, 248, 501–506.

Conroy, N. A., Wylie, E. M., & Powell, B. A. (2016). A Novel Method for Tracer Concentration Plutonium(V) Solution Preparation. *Analytical Chemistry*, *88*(8), 4196–4199.

Conroy, N. A., Zavarin, M., Kersting, A. B., & Powell, B. A. (2017). Effect of Natural Organic Matter on Plutonium Sorption to Goethite. *Environmental Science and Technology*, *51*(1), 699–708.

Davis, S. N., & Dewiest, R. J. M. (1966). *Hydrogeology*. (John Wiley & Sons, Ed.).

DeVol, T. A., & Husson, S. M. (2018). *Final Report to Defense Threat Reduction Agency*.

DeVol, T. A., Roane, J. E., Williamson, J. M., Duffey, J. M., & Harvey, J. T. (2000). Development of Scintillating Extraction Media for Separation and Measurement of Charged-Particle-Emittinig Radionuclides in Aqueous Solutions. *Radioactivity & Radiochemistry*, *11*(1), 34–46.

Dulanská, S., Remenec, B., Mátel, L., & Durkot, E. (2012). Rapid determination of : *Radioanal Nucl Chem*, *293*(1), 81–85.

Dulanská, S., Remenec, B., Mátel, Ľ., & Galanda, D. (2011). The selective separation of Pu isotopes using molecular recognition technology product AnaLig® Pu02 gel and

extraction chromatography TRU® resin. *Journal of Radioanalytical and Nuclear Chemistry*, *287*(3), 841–845.
Duval, C. E., DeVol, T. A., & Husson, S. M. (2016a). Evaluation of resin radius and column diameter for the implementation of extractive scintillating resin in flow-cell detectors. *Journal of Radioanalytical and Nuclear Chemistry*, *307*(3), 2253–2258.
Duval, C. E., DeVol, T. A., & Husson, S. M. (2016b). Extractive scintillating polymer sensors for trace-level detection of uranium in contaminated ground water. *Analytica Chimica Acta*, *947*, 1–8.
Duval, C. E., DeVol, T. A., Wade, E. C., Seliman, A. F., Bliznyuk, V. N., & Husson, S. M. (2016). Stability of polymeric scintillating resins developed for ultra-trace level detection of alpha- and beta-emitting radionuclides. *Journal of Radioanalytical and Nuclear Chemistry*, *310*(2), 583–588.
EPA, U. (2000). Radionuclides Rule 66. *Federal Register*, *65*(236). Retrieved from https://www.epa.gov/dwreginfo/radionuclides-rule
Ewing, R. C. (1999). Nuclear waste forms for actinides. *Proceedings of the National Academy of Sciences of the United States of America*, *96*(7), 3432–3439.
Flanary, J. . (1954). The Purex Process at Oak Ridge National Laboratory. *Reactor Science and Technology*.
Gokmen, M. T., & Du Prez, F. E. (2012). Porous polymer particles - A comprehensive guide to synthesis, characterization, functionalization and applications. *Progress in Polymer Science (Oxford)*.
Gostic, J. M. (2009). *Evaluation of extraction chromatography resins for rapid actinide analysis*.
Grate, J. W., Egorov, O. B., O'Hara, M. J., & DeVol, T. A. (2008). Radionuclide sensors for environmental monitoring: From flow injection solid-phase absorptiometry to equilibrium-based preconcentrating minicolumn sensors with radiometric detection. *Chemical Reviews, 108(2), 543-562*.
Harvey, J. T., Williamson, J. M., Duffey, J. M., DeVol, T. A., & Roane, J. E. (1998). *Development of a Radiochemical Sensor for Environmental Applications* (Final Report). Darien, IL: Eichrome Industries, Inc.
Hill, O. F., & Cooper, V. R. (1958). Scale-up Problems in the Plutonium Separations Program. *Industrial and Engineering Chemistry*, *50*(4), 599–602.
Hixon, A. E., & Powell, B. A. (2018). Plutonium environmental chemistry: mechanisms for the surface-mediated reduction of Pu(V / VI). *Environmental Science: Processes & Impacts*, *20*(10), 1306–1322.
Horwitz, E. P., Dietz, M. L., Chiarizia, R., Diamond, H., Maxwell, S. L., & Nelson, M. R. (1995). Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions. *Analytica Chimica Acta*, *310*(1), 63–78.
Horwitz, E. P., McAlister, D. R., & Dietz, M. L. (2006). Extraction chromatography versus solvent extraction: How similar are they? In *Separation Science and Technology*, 41, 2163–2182. Taylor & Francis Group.
IBC Advanced Technologies, I. *ANALIG ® GEL DATA SHEET CATALOG NUMBER*

PU-02.
Izatt, S., Bruening, R., Krakowiak, K., & Izatt, R. (2003). The selective separation of anions and cations in nuclear waste using commercially available molecular recognition technology products. *Proceedings of WM*, (16), 16–23.
Kaplan, D. I., Powell, B. A., Demirkanli, D. I., Fjeld, R. A., Molz, F. J., Serkiz, S. M., & Coates, J. T. (2004). Influence of Oxidation States on Plutonium Mobility during Long-Term Transport through an Unsaturated Subsurface Environment. *Environmental Science and Technology*, *38*(19), 5053–5058.
Katz, J. ., Seaborg, G. ., & Morss, L. . (1986). *The Chemistry of the Actinide Elements* (2nd ed, vo). New York: Chapman and Hall.
Kazi, Z. H., Cornett, J. R., Zhao, X., & Kieser, L. (2014). Americium and plutonium separation by extraction chromatography for determination by accelerator mass spectrometry. *Analytica Chimica Acta*, *829*, 75–80.
Kersting, A. B. (2013). Plutonium transport in the environment. *Inorganic Chemistry*, *52*(7), 3533–3546.
Kersting, A. B., Efurd, D. W., Finnegan, D. L., Rokop, D. J., Smith, D. K., & Thompson, J. L. (1999). Migration of plutonium in ground water at the Nevada Test Site. *Nature*, *397*(6714), 56–59.
Kersting, A., & Zavarin, M. (2011). Actinide Nanoparticle Research. In *Actinide Nanoparticle Research* (p. 399). Berlin, Germany: Springer-Verlag.
Kobashi, A., Choppin, G. R., & Morse, J. W. (1988). A Study of Techniques for Separating Plutonium in Different Oxidation States. *Radiochimica Acta*, *43*(4), 211–216.
Kobashi, A., Tominaga, T., Hoshi, M., Yonezawa, C., & Saeki, M. (1993). Separation of actinoid(III) and actinoid(IV) by solvent extraction and adsorption. *Journal of Alloys and Compounds*, *193*(1–2), 107–109.
Langmuir, D. (1997). *Aqueous Environmental Geochemistry*. Upper Sadle.
Matyjaszewski, K. (2016). Matyjaszewski Polymer Group: ATRP from Surfaces. Retrieved February 4, 2019, from https://www.cmu.edu/maty/atrp-how/procedures-for-initiation-of-ATRP/atrp-from-surfaces.html
Maxwell, S. L. (2006). Rapid column extraction method for actinides and 89/90 Sr in water samples. *Journal of Radioanalytical and Nuclear Chemistry*, *267*(3), 537–543.
Nash, K. L., Cleveland, J. M., & Rees, T. F. (1988). Speciation patterns of actinides in natural waters: a laboratory investigation. *Journal of Environmental Radioactivity*, *7*(2), 131–157.
Neu, B. M. P., Hoffman, D. C., Roberts, K. E., Nitsche, H., Silva, R. J., Solubility, P., & Groundwater, S. (1994). Comparison of Chemical Extractions and Laser Photoacoustic Spectroscopy for the Determination of Plutonium Species in Near-Neutral Carbonate Solutions. *Radiochimica Acta*, *258*(s1), 251–258.
PerkinElmer. (2007). Liquid Scintillation Counting | Application Support Knowledgebase | Lab Products & Services | PerkinElmer. Retrieved December 1, 2018, from http://www.perkinelmer.com/lab-products-and-services/application-support-knowledgebase/radiometric/liquid-scintillation-counting.html#Liquidscintillationcounting-Liquidscintillationcountingtheory

Powell, B. A., Fjeld, R. A., Kaplan, D. I., Coates, J. T., & Serkiz, S. M. (2004). Pu(V)O2+ adsorption and reduction by synthetic magnetite (Fe3O4). *Environmental Science and Technology*, *38*(22), 6016–6024.

Powell, B., & Kersting, A. (2008). Development of a Composite Non-Electrostatic Surface Complexation Model Describing Plutonium Sorption to Aluminosilicates. *Lawrence Livermore*

Roane, J. E., & DeVol, T. A. (2002). Simultaneous separation and detection of actinides in acidic solutions using an extractive scintillating resin. *Analytical Chemistry*, *74*(21), 5629–5634. http://doi.org/10.1021/ac026050z

Rose, A., Hawkes, H., & Webb, J. (1979). *Geochemistry in Mineral Exploration,* 657. London: Academic press.

Runde, W., Conradson, S. D., Wes Efurd, D., Lu, N. P., VanPelt, C. E., & Tait, C. D. (2002). Solubility and sorption of redox-sensitive radionuclides (Np, Pu) in J-13 water from the Yucca Mountain site: Comparison between experiment and theory. *Applied Geochemistry*, *17*(6), 837–853.

Runde, W., & Neu, M. P. (2011). Actinides in the Geosphere. In *The Chemistry of the Actinide and Transactinide Elements,* 3475–3593. Dordrecht: Springer Netherlands.

Saito, A., & Choppin, G. R. (1983). Separation of actinides in different oxidation states from neutral solutions by solvent extraction. *Analytical Chemistry*, *55*(Iv), 2454–2457.

Santschi, P. H., Roberts, K. A., & Guo, L. (2002). Organic nature of colloidal actinides transported in surface water environments. *Environmental Science and Technology*, *36*(17), 3711–3719.

Sasaki, Y., & Choppin, G. R. (1996). Solvent Extraction of Eu, Th, U, Np and Am with N, N'-Dimethyl-N,N'-dihexyl-3-oxapentanediamide ans Its Analogous Compounds. *Analytical Science*, *12*(2), 225–230.

Sasaki, Y., Sugo, Y., & Tachimori, S. (2000). Actinide separation with a novel tridentate ligand, diglycolic amide for application to partitioning process. In *In Proceedings of International Conference ATALANTE*, 1–6.

Schramke, J. A., Rai, D., Fulton, R. W., & Choppin, G. R. (1989). Determination of aqueous plutonium oxidation states by solvent extraction. *Journal of Radioanalytical and Nuclear Chemistry Articles*, *130*(2), 333–346.

Seliman, A. F. (2012). Affinity and removal of radionuclides mixture from low-level liquid waste by synthetic ferrierites. *Journal of Radioanalytical and Nuclear Chemistry*, *292*(2), 729–738.

Seliman, A. F., Bliznyuk, V. N., & DeVol, T. A. (2017). Development of stable extractive scintillating materials for real-time quantification of radiostrontium in aqueous solutions. *Journal of Radioanalytical and Nuclear Chemistry*, *314*(2), 743–751.

Seliman, A. F., Bliznyuk, V. N., Husson, S. M., & DeVol, T. A. (2015). Development of polymerizable 2-(1-naphthyl)-5-phenyloxazole scintillators for ionizing radiation detection. *J. Mater. Chem. C*, *3*(27), 7053–7061.

Silva, R. J., & Nitsche, H. (1995). Actinide Environmental Chemistry. *Radiochimica Acta*, *7071*, 377–396.

Turekian, K. K. (1977). The fate of metals in the oceans. *Geochimica et Cosmochimica Acta*, *41*(8), 1139–1144.

Van Hecke, K., & Modolo, G. (2004). Separation of actinides from Low Level Liquid Wastes (LLLW) by extraction chromatography using novel DMDOHEMA and TODGA impregnated resins. *Journal of Radioanalytical and Nuclear Chemistry*, *261*(2), 269–275.

Wang, H., Kang, J., Liu, H., & Qu, J. (2009). Preparation of organically functionalized silica gel as adsorbent for copper ion adsorption. *Journal of Environmental Sciences*, *21*(11), 1473–1479.